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Prepared by

Ronald L. Hershey, Wyatt Fereday, and James M. Thomas

Submitted to

Nevada Field Office
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Las Vegas, Nevada

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ABSTRACT

Dissolved inorganic carbon (DIC) carbon-14 (^{14}C) ages must be corrected for complex chemical and physical reactions and processes that change the amount of ^{14}C in groundwater as it flows from recharge to downgradient areas. Because of these reactions, DIC ^{14}C can produce unrealistically old ages and long groundwater travel times that may, or may not, agree with travel times estimated by other methods. Dissolved organic carbon (DOC) ^{14}C ages are often younger than DIC ^{14}C ages because there are few chemical reactions or physical processes that change the amount of DOC ^{14}C in groundwater.

However, there are several issues that create uncertainty in DOC ^{14}C groundwater ages including limited knowledge of the initial (A_0) DOC ^{14}C in groundwater recharge and potential changes in DOC composition as water moves through an aquifer. This study examines these issues by quantifying A_0 DOC ^{14}C in recharge areas of southern Nevada groundwater flow systems and by evaluating changes in DOC composition as water flows from recharge areas to downgradient areas. The effect of these processes on DOC ^{14}C groundwater ages is evaluated and DOC and DIC ^{14}C ages are then compared along several southern Nevada groundwater flow paths.

Twenty-seven groundwater samples were collected from springs and wells in southern Nevada in upgradient, midgradient, and downgradient locations. DOC ^{14}C for upgradient samples ranged from 96 to 120 percent modern carbon (pmc) with an average of 106 pmc, verifying modern DOC ^{14}C ages in recharge areas, which decreases uncertainty in DOC ^{14}C A_0 values, groundwater ages, and travel times.

The HPLC spectra of groundwater along a flow path in the Spring Mountains show the same general pattern indicating that the DOC compound composition does not change along this flow path. Although DOC concentration decreases from recharge-area to downgradient groundwater, the organic compounds are similar, indicating that DOC ^{14}C is unaffected by other processes such as microbial degradation.

A small amount of organic carbon was leached from crushed volcanic and carbonate aquifer outcrop rock in rock-leaching experiments. The leached DOC was high in ^{14}C (75 pmc carbonate rocks, 91 pmc volcanic) suggesting that the leached DOC likely came from microbes in the rock samples. The small amount of DOC and high ^{14}C indicates that the amount of old organic carbon in these rocks is low so there should be minimal impact on groundwater DOC ^{14}C ages.

Based on the results from this study, DOC ^{14}C ages do not require additional corrections. Several correction models were applied to DIC ^{14}C ages to correct for water-rock reactions along two carbonate and two volcanic flow paths and the corresponding travel times were compared to DOC ^{14}C travel times. The DOC ^{14}C travel times were hundreds to thousands of years shorter than uncorrected and corrected DIC ^{14}C travel times except for the upper section of one carbonate flow path. DOC ^{14}C travel times ranged from 400 to 5,400 years as compared to DIC ^{14}C that ranged from modern to 20,900 years. The DIC ^{14}C ages are greatly influenced by carbonate mineral and gas reactions and other processes such as matrix diffusion, isotope exchange, or adsorption, which are not always adequately accounted for in DIC ^{14}C groundwater age correction models.

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LIST OF ACRONYMS

^{13}C	carbon-13
^{14}C	carbon-14
DI	deionized
^2H	deuterium
DIC	dissolved inorganic carbon
DOC	dissolved organic carbon
A_0	initial ^{14}C in groundwater recharge
NaCl	halite
HPLC	high performance liquid chromatography
HCl	hydrogen chloride
HSU	hydrostratigraphic unit
km	kilometers
LCA	lower carbonate aquifer
LC/MS	liquid chromatograph/mass spectrometer
μm	micron
ml	milliliter

mmol/kg	millimoles per kilogram
NNSS	Nevada National Security Site
¹⁸ O	oxygen-18
pmc	percent modern carbon
‰	permil
H ₃ PO ₄	phosphoric acid
KMnO ₄	potassium permanganate
SOM	sedimentary organic matter
SiO ₂	silica
Stdv	standard deviation
SOP	standard operating procedure
TDS	total dissolved solids
UNR	University of Nevada, Reno
yrs	years

INTRODUCTION

Groundwater ages have been used to validate and constrain numerical models of groundwater flow at the Nevada National Security Site (NNSS). However, dissolved inorganic carbon (DIC) carbon-14 (^{14}C) data often overestimate groundwater ages because of the complex chemical and physical reactions that change the amount of ^{14}C in groundwater as it flows from recharge areas to downgradient aquifers (Thomas *et al.*, 1996; 2002; Hershey *et al.*, 2005; 2008; Kwicklis *et al.*, 2005; Farnham *et al.*, 2006; Rose *et al.*, 2006). These reactions must be accounted for to correct groundwater DIC ^{14}C ages. Difficulties in quantifying the changes in DIC ^{14}C by these chemical and physical reactions during groundwater flow can result in unrealistically old ages and longer groundwater travel times that may, or may not, support travel times generated by other methods (e.g., Stoller-Navarro Joint Venture, 2006; 2009; Navarro Intera, 2010; 2013). The Phase I Western Pahute Mesa flow and transport modeling highlighted inconsistencies between numerical model groundwater flow rates and flow rates calculated using DIC ^{14}C (Stoller-Navarro Joint Venture, 2009, Appendix D). In this case, numerical model flow rates were generally much faster than DIC ^{14}C rates. More recently, observed radionuclide activities in well ER-EC-11 downgradient from the Benham underground test suggest even faster groundwater flow rates in this area of western Pahute Mesa (Charles Russell, Desert Research Institute [DRI], personal communication, 2015).

Groundwater ages determined using dissolved organic carbon (DOC) ^{14}C data are often younger than DIC ^{14}C ages because there are very few chemical reactions or physical processes that change the amount of DOC ^{14}C in groundwater samples (Murphy *et al.*, 1989a; Murphy *et al.*, 1989b; Wassenaar *et al.*, 1991; Purdy *et al.*, 1992; Thomas, 1996; Stoller-Navarro Joint Venture, 2006). These younger DOC ^{14}C groundwater ages often produce groundwater travel times that can be more consistent with travel times determined by other methods than the DIC ^{14}C travel times (Fereday, 2013; Hershey *et al.*, 2008; Rose *et al.*, 2006; Farnham *et al.*, 2006; Hershey *et al.*, 2005; Thomas *et al.*, 2002; Morse, 2002; Winograd *et al.*, 1997; Thomas, 1996). However, there are several issues that create uncertainty in DOC ^{14}C groundwater ages in addition to normal measurement uncertainty (e.g., sampling variability, analytical uncertainty, etc.). These include limited knowledge of the “initial” (A_0) DOC ^{14}C in groundwater recharge, potential changes in DOC composition as water moves through an aquifer (addition, removal, or degradation of DOC), and water-aquifer matrix interaction (matrix diffusion and/or adsorption of DOC ^{14}C). This study examines two of these issues by quantifying A_0 DOC ^{14}C in recharge areas of southern Nevada groundwater flow systems and by evaluating changes in dissolved organic carbon composition as water flows from recharge areas to downgradient areas. The effect of these on DOC ^{14}C groundwater ages in southern Nevada flow systems is also evaluated. Another process, water-aquifer matrix interaction, is addressed in a separate report (Hershey *et al.*, 2016). This study will help reduce uncertainty in modeling of contaminant transport by providing another independent method to estimate groundwater travel times.

Description of the Problem

Most ^{14}C groundwater ages are determined using DIC. Chemical reactions, isotopic exchange, and matrix diffusion can affect DIC ^{14}C dates by adding “dead carbon” (carbon that contains no ^{14}C) to the water and/or removing ^{14}C from the water. As a result, DIC ^{14}C

groundwater ages must be corrected using models that account for chemical and physical processes as groundwater moves from recharge areas to the downgradient point of sampling. These corrections require chemical and isotopic analyses of aquifer rocks and groundwater, knowledge of the chemical and isotopic reactions that occur in the aquifer, and knowledge of the amount of matrix diffusion (Clark and Fritz, 1997). Conversely, it is typically assumed that DOC ^{14}C groundwater ages do not require any correction for chemical reactions (Nakata *et al.*, 2013; Burr *et al.*, 2001; Ivanovich *et al.*, 1996; Aravena *et al.*, 1995; Artinger *et al.*, 1996; Aravena and Wassenaar, 1993; Purdy *et al.*, 1992; Wassenaar *et al.*, 1991; Drimmie *et al.*, 1991, Wassenaar *et al.*, 1989, Murphy *et al.*, 1989a, 1989b; Murphy, 1987). Consequently, DOC ^{14}C ages provide an opportunity to obtain more accurate groundwater ages than derived from DIC ^{14}C (Nakata *et al.*, 2013; Fereday, 2013; Morse, 2002; Burr *et al.*, 2001; Ivanovich *et al.*, 1996; Thomas, 1996; Aravena *et al.*, 1995; Artinger *et al.*, 1996; Aravena and Wassenaar, 1993; Purdy *et al.*, 1992; Wassenaar *et al.*, 1991; Drimmie *et al.*, 1991, Wassenaar *et al.*, 1989, Murphy *et al.*, 1989a, 1989b; Murphy, 1987). However, there are some processes that may affect DOC ^{14}C ages and these processes are poorly characterized in southern Nevada aquifers. An evaluation of potential effects on some of these processes on DOC ^{14}C ages may help to explain differences between DIC ^{14}C and DOC ^{14}C groundwater ages.

Similar to calculating groundwater ages with DIC ^{14}C , DOC ^{14}C age calculations require knowledge of ^{14}C A_0 in groundwater recharge (i.e., the amount of ^{14}C in the water at the time of recharge). The A_0 values for calculating DOC ^{14}C ages are not well documented for recharge areas important to southern Nevada groundwater and they cannot be assumed to be 100 percent modern carbon (pmc) because not all organic carbon encountered by recharging waters is modern in age. Before this study, limited available data indicated that the DOC ^{14}C of recharge area groundwater in southern Nevada falls within a range of 60 to 100 pmc. For example, Cold Creek Spring in the Spring Mountains has a DOC ^{14}C value of 91 pmc (Thomas, 1996), whereas groundwater in shallow wells UE-29a #1 and #2 in Fortymile Wash have DOC ^{14}C values of 63 and 67 pmc (Thomas *et al.*, 2002). This range in potential DOC ^{14}C A_0 values introduces significant uncertainty to DOC ^{14}C ages, so DOC ^{14}C A_0 values in recharge areas need to be quantified.

The DOC ^{14}C groundwater dating method assumes that no organic carbon is added to groundwater as it moves through an aquifer. In most aquifers of southern Nevada, any organic carbon in the aquifer matrix is very old and devoid of ^{14}C , so any addition of organic carbon from an aquifer matrix to groundwater would result in a DOC ^{14}C groundwater age that is older than the actual groundwater age. The DOC ^{14}C groundwater dating method also assumes that the organic carbon in the recharge areas is the same organic carbon collected at downgradient wells and springs. The DOC composition of groundwater in the recharge areas may degrade and transform by in-situ biological processes as groundwater flows through aquifers, possibly resulting in artificially younger DOC groundwater ages.

However, groundwater travel-times in the lower carbonate aquifer (LCA) in southern Nevada calculated using DOC ^{14}C ages (Morse, 2002; Thomas, 1996) are consistent with travel times calculated using hydrogeologic data (Thomas *et al.*, 1996) and with abrupt shifts in the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ record in precipitated calcite in Devils Hole (Winograd *et al.*, 2006; 1997). Winograd *et al.* (2006; 1997) estimated the travel time of recharge water from the Spring Mountains to Devils Hole (approximately 80 kilometers [km]) to be between less than

1000 and less than 2000 years ([yrs], average groundwater velocity greater than 40 to greater than 80 km/yr). These groundwater travel times in the LCA suggest that DOC ^{14}C groundwater ages are not significantly affected by the DOC processes discussed above.

To address potential issues associated with DOC ^{14}C groundwater dating: 1) DOC ^{14}C A_0 values for southern Nevada were quantified, 2) the organic carbon content of southern Nevada aquifer rocks was evaluated, 3) identification of the specific organic compounds in southern Nevada groundwater and changes in these compounds as water flows through the aquifers was attempted, 4) the impact of the results of these investigations on DOC ^{14}C groundwater ages was evaluated, and 5) DOC ^{14}C and DIC ^{14}C groundwater ages were compared along several well-characterized groundwater flow paths in southern Nevada and discrepancies between these ages were evaluated.

Determination of DOC ^{14}C A_0 Values

Spring or shallow groundwater samples from the NNSS and other nearby recharge areas (Spring Mountains, Sheep Range, Kawich Range) were collected and analyzed for both DOC ^{14}C and DIC ^{14}C . When possible, samples were collected from sites with historical water chemistry and isotopic data to assist in interpretation. Additionally, sites were screened to ensure that samples are representative of recent groundwater recharge. Criteria for being a recharge site include DIC ^{14}C greater than 85 pmc and detectable tritium activity.

Determination of Organic Carbon Content in Aquifer Rocks

Ideally, core samples from the aquifers would be used for this analysis; however, cores are contaminated with drilling fluids, which often contain organic additives, so outcrop samples were used instead. Aquifer rock outcrop samples were collected from the NNSS, Spring Mountains, and the Sheep Range to test for the presence of very old, ^{14}C free, organic carbon that could dilute groundwater DOC ^{14}C , and therefore, increase DOC ^{14}C ages. The amount of organic carbon in the rock samples was measured by crushing the samples and leaching them in DOC-free, deionized (DI) water to dissolve any organic carbon present in the core samples. Exterior surfaces of the rock samples were removed and only fresh rock matrix was used for leaching experiments.

Identification of Organic Compounds in Groundwater

Dissolved organic carbon is any aqueous organic carbon compound that passes through a 0.45 micron (μm) filter. The organic compounds can include a wide range of naturally occurring acids, bases, DNA, proteins, and polymers. The DOC compounds present in southern Nevada aquifers and their respective molecular sizes are not currently known. Ideally, specific DOC compounds in groundwater can be identified and a comparison made between upgradient and downgradient groundwater to evaluate whether the DOC compound in groundwater have changed along the flow path.

Three springs and one well were analyzed to identify the DOC compounds present. These samples were collected along a representative flow path from recharge areas in the Spring Mountains to the adjacent valley floor. Groundwater samples were collected from Deer Creek Spring #1 and McFarland Spring in the upgradient recharge area of the Spring Mountains, from Cold Creek Spring, which is midgradient along this flow path on an alluvial fan of the Spring Mountains, and from Indian Springs Prison Well #4 at the downgradient part of this flow path near the valley floor. Groundwater samples were then concentrated by

rotary evaporation to recover enough DOC to try and identify the organic compounds present. The DOC compound identification was conducted by Dr. Glenn Miller at the University of Nevada, Reno (UNR) and Dr. David Quillici of UNR's Nevada Proteomics Center.

Comparison of DOC ^{14}C Ages with DIC ^{14}C Ages along Groundwater Flow Paths

Groundwater samples collected for this study were analyzed for DIC ^{14}C and DOC ^{14}C . These data were then used to calculate groundwater DIC ^{14}C ages and DOC ^{14}C ages. Dissolved organic carbon ^{14}C groundwater ages were calculated using the newly obtained DOC ^{14}C A_0 values. The DOC ^{14}C groundwater ages were compared with uncorrected and corrected DIC ^{14}C ages along several volcanic and carbonate aquifer flow paths.

Study Area and Groundwater Samples

Twenty-seven groundwater samples were collected from springs and wells from the NNSS, Spring Mountains, Sheep Range, Kawich Range, and Ash Meadows in the Amargosa Desert of southern Nevada (Figure 1; Table 1; Appendix A). Sample type and location are summarized in Appendix A. Fourteen upgradient samples were collected from 13 high-altitude springs and one high altitude well that are recharged locally. Volcanic springs are located on the NNSS and Kawich Range. Carbonate springs are high-elevation locations in the Spring Mountains and Sheep Range. One upgradient location is a high-altitude well in the Spring Mountains. Ten downgradient locations (discharge-area springs and wells) include seven lower elevation wells and three regional springs. Two downgradient wells are at the base of the Spring Mountains and six are on the NNSS. Three downgradient springs at Ash Meadows, Fairbanks, Crystal Pool, and Point of Rocks springs, are regional springs with relatively long flow paths (Winograd and Thordarson, 1975; Thomas *et al.*, 1996; Morse, 2002). Historical data from well UE-19h (not sampled for this study) are used for flow-path travel-time modeling (UGTA, 2008). Three samples, Cold Creek Spring, Tramp Spring, and well UE-29a #2 were classified as “midgradient” based on their hydrologic setting and ^{14}C less than 100 pmc.

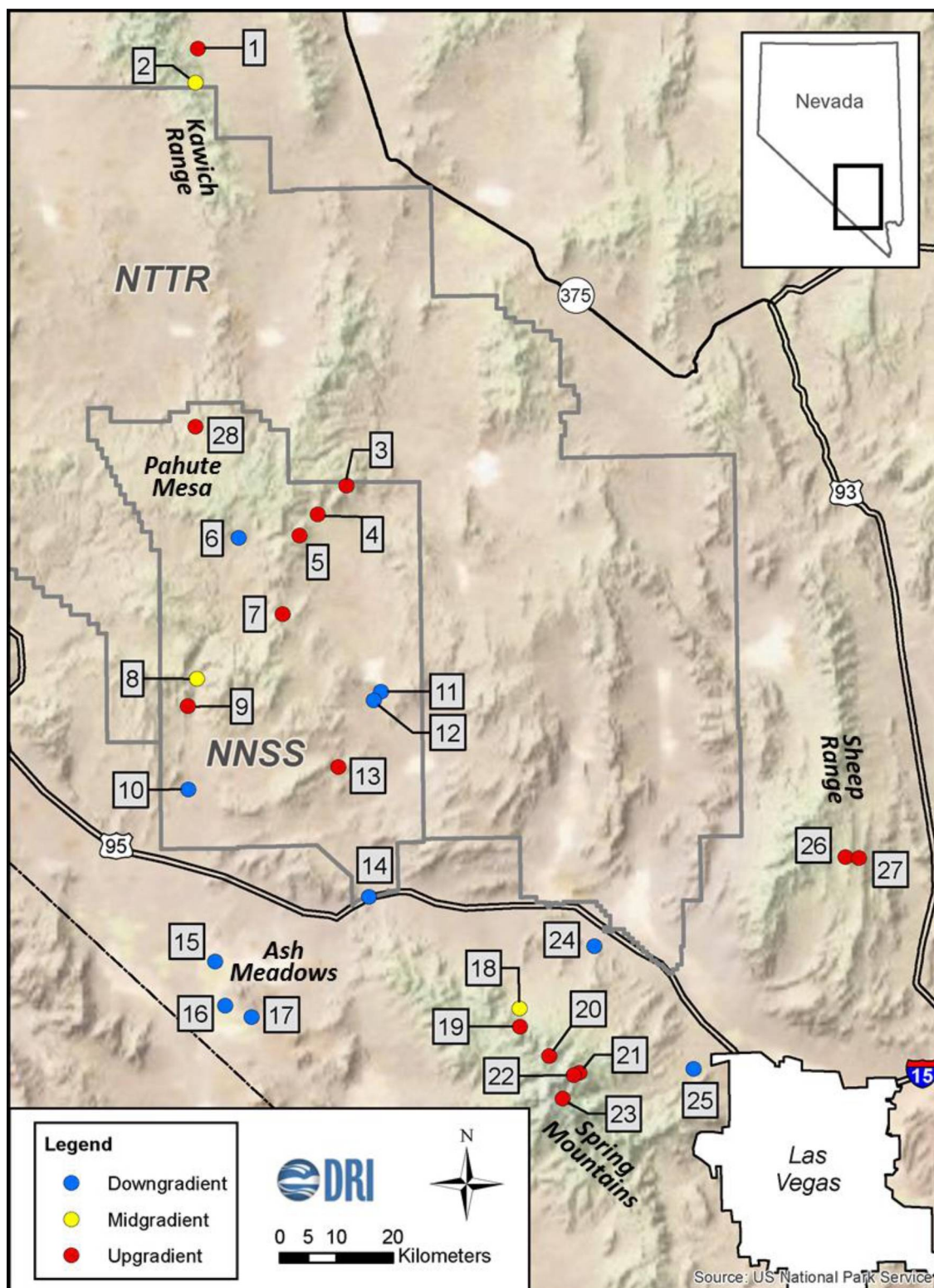


Figure 1. Groundwater sample locations in southern Nevada separated into up-, mid-, and downgradient locations. NNSS = Nevada National Security Site. NTTR = Nevada Test and Training Range.

Table 1. Groundwater sample locations (Figure 1); their hydrologic site designation as up-, mid-, or downgradient; the geographical region where the spring or well is located; and the rock type the spring issues from or the well is completed in.

#	Location	Latitude	Longitude	x_utm	y_utm	Gradient	Region	Rock Type
1	Unnamed Spring East Kawich	37 56 40.0	116 21 50.0	555891.2	4199841.8	up	Kawich Range	volcanic
2	Tramp Spring	37 53 26.5	116 22 09.3	555460.5	4193874.9	mid	Kawich Range	volcanic
3	John's Spring	37 14 49.9	116 04 27.5	582099.2	4122694.9	up	NNSS	volcanic
4	White Rock East Spring	37 12 05.7	116 07 53.4	577072.5	4117588.1	up	NNSS	volcanic
5	Captain Jack Spring	37 10 06.8	116 10 06.9	573813.8	4113896.1	up	NNSS	volcanic
6	Water Well 8	37 09 56.0	116 17 21.0	563110.2	4113474.8	down	NNSS	volcanic
7	Tippipah Spring	37 02 34.9	116 12 11.6	570854.8	4099941.2	up	NNSS	volcanic
8	UE-29a #2	36 56 28.7	116 22 26.0	555751.0	4088543.7	mid	NNSS	volcanic
9	Cottonwood Spring	36 53 52.9	116 23 34.4	554091.7	4083730.9	up	NNSS	volcanic
10	J-12 Water Well	36 45 54.0	116 23 34.0	554194.4	4068975.5	down	NNSS	volcanic
11	Water Well C-1	36 55 07.0	116 00 34.0	588230.8	4086301.9	down	NNSS	volcanic
12	Water Well 4	36 54 18.0	116 01 26.0	586959.6	4084778.6	down	NNSS	volcanic
13	Cane Spring	36 47 55.6	116 05 42.1	580734.5	4072932.9	up	NNSS	volcanic
14	Army #1 Water Well	36 35 30.0	116 02 14.0	586121.3	4050007.5	down	NNSS	volcanic
15	Fairbanks Spring	36 29 25.7	116 20 31.5	558927.5	4038552.2	down	Ash Meadows	carbonate
16	Crystal Pool Spring	36 25 12.8	116 19 23.5	560674.0	4030771.6	down	Ash Meadows	carbonate
17	Point of Rocks Spring	36 24 05.8	116 16 16.3	565351.4	4028741.2	down	Ash Meadows	carbonate
18	Cold Creek Spring	36 24 41.3	115 44 37.7	612630.7	4030320.4	mid	Spring Mountains	carbonate
19	McFarland Spring	36 22 54.7	115 44 38.0	612664.7	4027037.3	up	Spring Mountains	carbonate
20	Upper Mack's Canyon Spring	36 20 07.0	115 41 11.0	617892.6	4021937.5	up	Spring Mountains	carbonate
21	Deer Creek Spring #2	36 18 26.7	115 37 41.4	623162.2	4018919.2	up	Spring Mountains	carbonate
22	Deer Creek Spring #1	36 18 15.0	115 38 21.0	622179.4	4018545.0	up	Spring Mountains	carbonate
23	Echo 4 Well	36 26 69.0	115 66 15.1	620230.0	4014383.0	up	Spring Mountains	carbonate
24	Indian Springs Prison Well #4	36 30 30.9	115 35 41.0	625839.1	4041279.9	down	Spring Mountains	carbonate
25	Mifflin Well	36 18 38.4	115 24 12.8	643322.9	4019589.4	down	Spring Mountains	carbonate
26	Mormon Well Spring	36 38 39.1	115 05 47.2	670167.1	4057090.1	up	Sheep Range	carbonate
27	Wamp Spring	36 38 30.7	115 04 11.2	672555.2	4056880.2	up	Sheep Range	carbonate
28	UE-19h	37 20 34.1	116 22 24.8	555487.6	4133086.0	up	NNSS	volcanic

METHODS

Sample Collection

Groundwater Samples

All groundwater samples were collected using separate, pre-cleaned, 0.45 μm filter cartridges and silicone tubing. Filter cartridges were flushed with DOC-free DI water for one hour in the laboratory, and then refrigerated until time of use. The tubing was purged for roughly 10 minutes with the sample water, then the filter cartridge was connected and the tubing and filter were purged together with at least 1 liter (L) of sample water prior to sample collection. Spring samples were collected with a peristaltic pump by inserting the silicone tubing as close to the spring orifice as possible. Wells were purged until roughly three-to-five well volumes had discharged prior to sample collection. The DOC ^{14}C samples were collected in 1 L, factory-cleaned and baked, amber glass bottles. Samples for DOC compound identification were collected in 4 L, factory-cleaned and baked, amber glass jugs. The DOC concentration samples were collected in 125 milliliter (mL), factory-cleaned and baked, amber glass bottles. Hydrogen ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) isotopic samples were collected in 30 mL, clear glass bottles with PolysealTM cone lids. Cation samples were collected in 250 mL, plastic bottles and acidified with reagent grade nitric acid (HNO_3). Anion samples were collected in 500 mL, plastic bottles. The DIC carbon ($\delta^{13}\text{C}$) isotope and ^{14}C samples were collected in separate 1 L, clear glass bottles with PolysealTM cone lids.

Rock Outcrop Samples

Seven volcanic and five carbonate outcrop rock samples were collected from the NNSS, Sheep Range, and Spring Mountains (Figure 2). These rocks were selected from known aquifer hydrostratigraphic units (HSUs) for the water-rock leaching experiments. Stratigraphic Unit Map Symbols and HSUs for each sample are listed in Table 2.

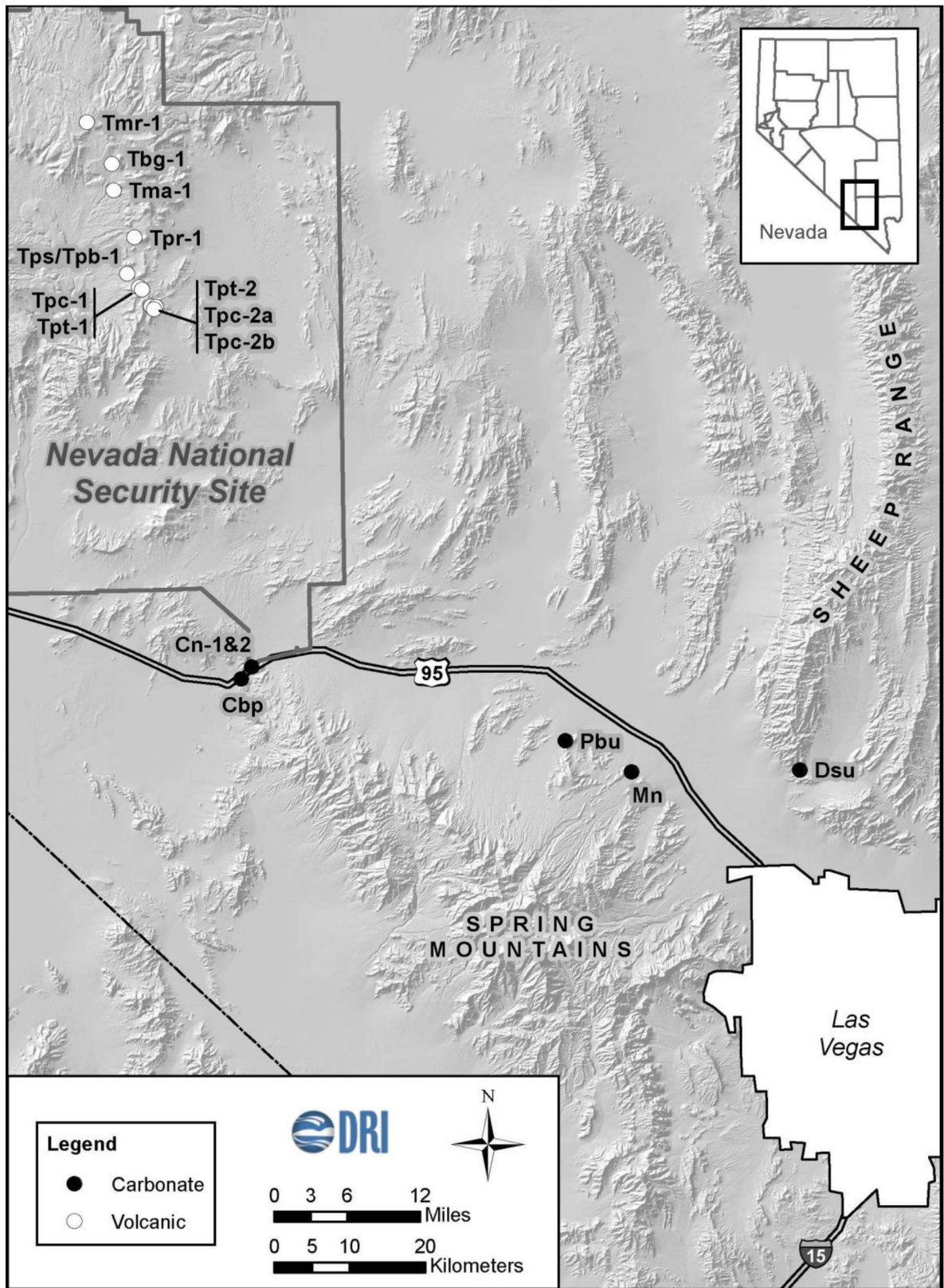


Figure 2. Aquifer rock outcrop sample locations.

Table 2. Aquifer rock outcrop sample locations with Stratigraphic Unit Map Symbols and corresponding Hydrostratigraphic Units (HSUs) from Figure 2.

Name	HSU(s)	Latitude	Longitude
Volcanic			
Tma-1	Timber Mountain welded-tuff aquifer	37°09'01.9"	116°15'53.7"
Tmr-1	Timber Mountain welded-tuff aquifer	37°13'53.8"	116°18'15.2"
Tps/Tpb-1	Scrugham Peak aquifer and Benham aquifer	37°03'02.9"	116°14'45.0"
Tpc-1	Tiva Canyon aquifer	37°01'53.6"	116°13'27.7"
Tpc-2a	Tiva Canyon aquifer	37°00'38.6"	116°12'14.0"
Tpc-2b	Tiva Canyon aquifer	37°00'28.7"	116°12'24.4"
Tpr-1	Paintbrush lava-flow aquifer	37°05'38.2"	116°14'04.2"
Tpt-1	Topopah Spring aquifer	37°02'04.4"	116°13'42.6"
Tpt-2	Topopah Spring aquifer	37°00'40.7"	116°12'38.1"
Tbg-1	Belted Range aquifer	37°10'53.9"	116°16'03.4"
Carbonate			
Pbu	Lower Carbonate Aquifer	36°29'16.7"	115°36'16.8"
Mm	Lower Carbonate Aquifer	36°26'59.1"	115°30'25.6"
Dsu	Lower Carbonate Aquifer	36°26'56.4"	115°15'32.5"
Cn-1&2	Lower Carbonate Aquifer	36°34'51.3"	116°03'58.3"
Cbp	Lower Carbonate Aquifer	36°34'00.2"	116°04'55.0"

DOC ¹⁴C Analysis

The DOC ¹⁴C analysis follows the DRI laboratory standard operating procedure ([SOP], DRI, 2014). One-liter groundwater samples were placed in clean glass evaporation vessels with 25 mL of phosphoric acid (H₃PO₄) to convert DIC in the sample to carbon dioxide (CO₂) gas, which was then removed by a vacuum pump (Figure 3). The samples were heated to 50 degrees Celsius (°C) with a heating mantle, connected to a vacuum line with cold traps containing ethanol chilled to below -10 °C to collect water vapor before the vacuum pump, and evaporated until only the H₃PO₄, dissolved solids, and DOC remained. The samples were then cooled to room temperature, 500 mg of potassium permanganate (KMnO₄) was added, and each sample was evacuated again. The sample vessels were then heated using a heat tape at 80 °C for about 12 hours to allow the KMnO₄ to completely oxidize the DOC to CO₂. Finally, the sample vessels were put on a high-vacuum line (pressure ≤ 10⁻⁵ Torr) where the CO₂ was separated from other gases and water vapor using a series of cold traps (Figure 4). The CO₂ gas samples were sent to the NSF-Arizona Accelerator Mass Spectrometry Facility at the University of Arizona where a graphite target was prepared and analyzed for ¹⁴C. A portion of the CO₂ was analyze for δ¹³C by isotope-ratio mass spectrometry.



Figure 3. Vacuum line with DOC water samples connected to cold traps for DIC CO₂ gas removal and evaporation.



Figure 4. High-vacuum line (pressure $\leq 10^{-5}$ Torr) where CO₂ from DOC samples is separated from other gases using a series of cold traps.

Water and Rock Chemistry and Isotopic Analyses

All water samples were analyzed for DOC concentration, major cations and anions, $\delta^2\text{H}$ and $\delta^{18}\text{O}$, DIC $\delta^{13}\text{C}$ and ^{14}C , and DOC $\delta^{13}\text{C}$ and ^{14}C . Dissolved organic carbon, cations, and anions were analyzed at the DRI's Water Analysis Laboratory in Reno, Nevada. Stable isotopic analyses ($\delta^2\text{H}$, $\delta^{18}\text{O}$, DIC $\delta^{13}\text{C}$) were conducted at the Nevada Stable Isotope Laboratory at the University of Nevada, Reno. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values are referenced to the Vienna Mean Standard Ocean Water standard and $\delta^{13}\text{C}$ values are referenced to the Vienna Pee Dee Belemnite standard. Water samples were analyzed for DIC ^{14}C , DOC $\delta^{13}\text{C}$, and DOC ^{14}C at the NSF-Arizona Accelerator Mass Spectrometry Facility at the University of Arizona.

DOC Compound Identification

Four liters of water samples from upgradient and midgradient springs and downgradient wells were concentrated using rotary evaporation (Figure 5). The samples were placed in 2 L, rotary-evaporation flasks that were pre-cleaned by overnight immersion in a 10 percent hydrogen chloride (HCl) acid bath, and then baked at 440 °C for 12 hours. Four-liter samples were reduced to approximately 15 mL, which were then collected in 125 mL, factory-cleaned and baked, amber glass bottles. Samples were analyzed by the Nevada Proteomics Center (University of Nevada, Reno [<http://www.unr.edu/proteomics>]) using tandem mass spectrometry on a Thermo Scientific LTQ Orbitrap ion-trap liquid chromatography mass spectrometer (LC/MS). A hydrophilic interaction chromatography (HILIC) column (PolyHYDROXYETHYL ATM, PolyLC, Inc.) was used with an initial 100 percent acetonitrile solvent that transitioned to 100 percent distilled-water solvent over the course of each run. This eluent arrangement delivers non-polar compounds first and the more polar compounds next as the percentage of water in the eluent increased to 100 percent in a high-performance, liquid chromatography (HPLC) run. Dissolved organic carbon-free DI water blanks were also run from the initial rotary-evaporation step through each HPLC run for quality control.



Figure 5. Rotary evaporator used to concentrate water samples for DOC compound identification.

Rock-leaching Experiment

Weathered surfaces of the five carbonate and seven volcanic outcrop rock samples were removed using a pre-cleaned rock saw lubricated with DOC-free DI water. Only pristine rock matrix with no visible cracks or fractures were used. The unweathered rocks were then cut into roughly 3 centimeter (cm) x 5 cm pieces, rinsed with DOC-free DI water, dried, and crushed using a pre-cleaned ceramic jaw crusher (Figure 6a-c). The rock saw and rock crusher were cleaned with soap and water, a DOC-free DI water rinse, ethanol, and a final DOC-free DI water rinse prior to use and in between crushing the two rock types.



Figure 6. (a) Cut rocks for jaw crusher; (b) crushed rock; (c) leaching crushed rock.

Equal volumes of approximately 200 mL (approximately 1,400 grams [g]) of each of the five crushed carbonate rocks were combined to make approximately 1 L of crushed rock that were then placed in a 4 L, factory-cleaned and baked, amber glass jug (reactor; Figure 6c). Three liters of DOC-free DI water was then added to the reactor. This procedure was repeated for the volcanic rocks using approximately 140 mL (approximately 1,100 g) from each of the seven units to attain 1 L of crushed rock. The procedure was repeated three times each for the carbonate and volcanic rocks for a total of six, 4 L reactors. Two 4 L reactors were also prepared with 3 L of DOC-free DI water as experiment blanks. The eight reactors were then shaken by hand to mix the crushed rock and water, and then placed in the refrigerator. The reactors were shaken once daily for five days. The leached water from the eight reactors was sampled after six days using a peristaltic pump, clean silicone tubing, and pre-cleaned 0.45 μm filter cartridges. From each reactor, 125 mL samples and 1 L samples were collected for DOC and DOC ^{14}C analyses, respectively.

DIC ^{14}C and DOC ^{14}C Flow-path Travel-time Modeling

Various correction models have been developed to correct DIC ^{14}C ages for processes that change the amount of DIC ^{14}C along groundwater flow paths; often each correction model produces a different radiocarbon age for the same flow path (e.g., Wassenaar *et al.*, 1991; Thomas *et al.*, 1996; Clark and Fritz, 1997). Correction models are designed to account for the dissolution and precipitation of carbonate minerals, changes in dissolved CO_2 , and/or carbon isotopic exchange and fractionation processes that often result in reductions in DIC ^{14}C and groundwater ages. Dissolved organic carbon ^{14}C ages may be significantly different than both uncorrected and corrected DIC ^{14}C ages for the same flow path; therefore, it is important to compare DIC ^{14}C and DOC ^{14}C ages and travel times along specific flow-paths to evaluate changes in ^{14}C by processes other than radiocarbon decay.

Four previously identified flow paths with water-rock reaction models (Stoller Navarro Joint Venture, 2009, Appendix D; Rose *et al.*, 2006; Kwicklis *et al.*, 2005; Thomas *et al.*, 2002; Hershey, 1989) were reexamined to calculate groundwater travel times in carbonate and volcanic aquifers (Figure 7) using both DIC ^{14}C and DOC ^{14}C . Carbonate-aquifer flow paths 1 and 2 each contain up-, mid-, and downgradient components. Flow path 1 considers high-elevation groundwater recharge in the Spring Mountains (upgradient

component represented by McFarland Spring) flowing midway down the flow path (midgradient component represented by Cold Creek Spring) and then midgradient groundwater flowing downgradient to the valley floor (downgradient component represented by Indian Springs Prison Well #4). Carbonate-aquifer flow path 2 examines flow in a different portion of the Spring Mountains where groundwater recharge (upgradient component Deer Creek Spring #1) flows to midgradient in the flow path (midgradient represented by Echo 4 Well) and then to the valley floor (downgradient component Mifflin Well). Echo 4 Well is actually located in the lower portion of the recharge area and would normally be considered as an upgradient location as defined in this report. For water-rock reaction modeling, it is used as a midgradient location because of its position downgradient of Deer Creek Spring #1 and because it has lower DIC ^{14}C than Deer Creek Spring #1.

Volcanic-aquifer flow path 3 considers mixing of Pahute Mesa groundwater (represented by well UE-19h) flowing to midgradient in the flow path (midgradient represented by well UE-29a #2), mixing with local recharge (represented by Cottonwood Spring), and then flowing to the downgradient portion of the flow path (downgradient represented by J-12 Water Well). Historical data from Well UE-19h were used as it was not sampled for this study. Recent reinterpretations of groundwater levels by Fenelon *et al.* (2015) suggest that Pahute Mesa groundwater no longer is thought to flow southward long this flow path. Despite this new revelation, the volcanic-aquifer flow path 3 is still considered in this study because previous studies (Stoller Navarro Joint Venture, 2009, Appendix D; Rose *et al.*, 2006; Kwicklis *et al.*, 2005; Thomas *et al.*, 2002) reported a possible flow path using water chemistry and isotopic data and water-rock reaction models, and because changes in DIC ^{14}C and DOC ^{14}C for this flow path are still useful to examine. Volcanic-aquifer flow path 4 considers point-to-point groundwater flow from local groundwater recharge (upgradient represented by Tippihah Spring) to downgradient groundwater in a volcanic aquifer (downgradient represented by Water Well 4).

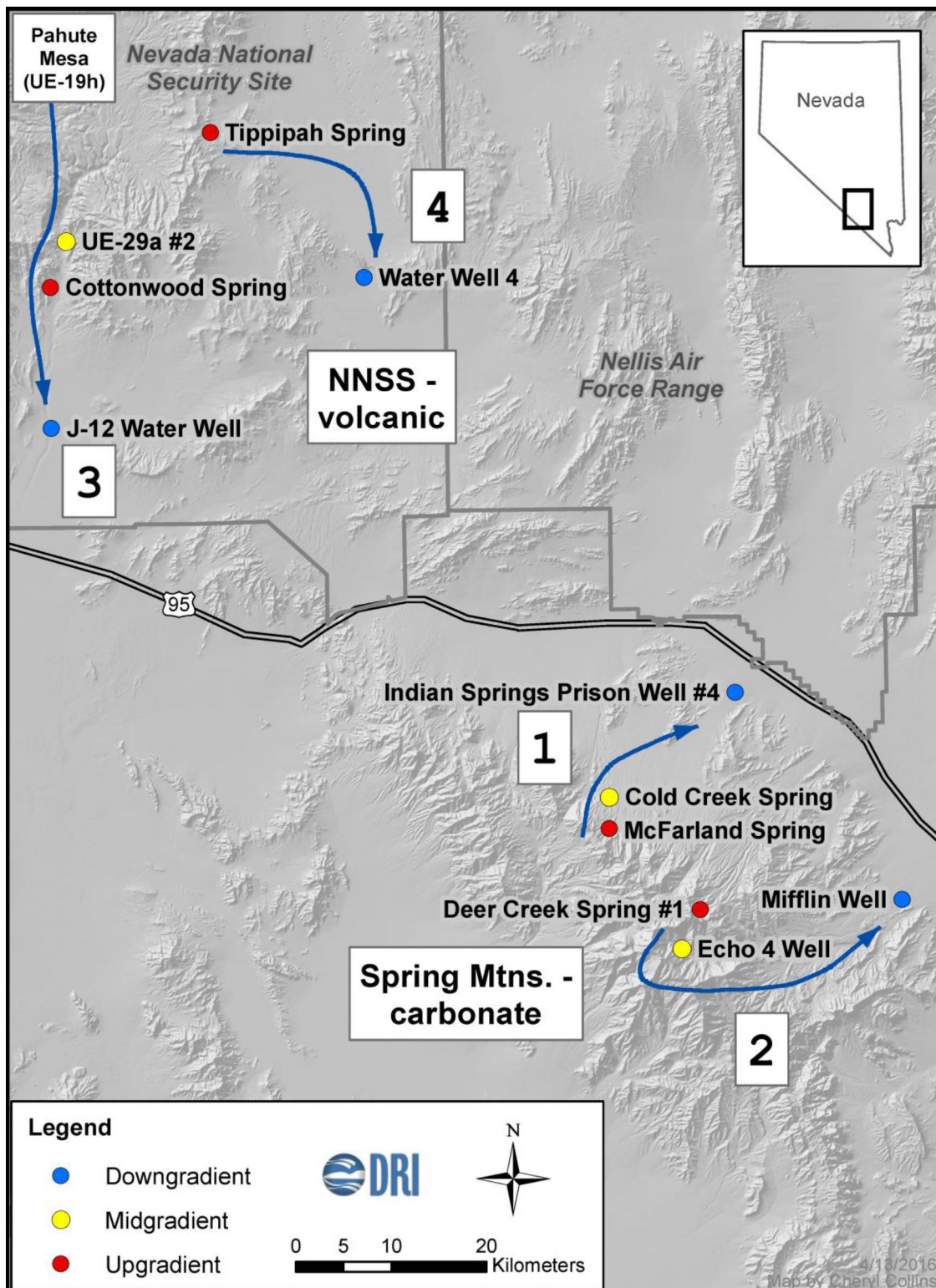


Figure 7. Carbon-14 modeled flow paths: carbonate-aquifer flow paths 1 and 2 in the Spring Mountains and volcanic-aquifer flow paths 3 and 4 at the NNSS. The chemical and isotopic composition of the up-, mid-, and downgradient components in the flow paths are represented by the specific spring and wells shown.

Consistent stable isotopic signatures (Table 3 $\delta^{18}\text{O}$ and $\delta^2\text{H}$) in flow paths 1, 2, and 4 suggest minimal mixing of other end-member waters during flow. In other words, essentially all of the downgradient water is recharged upgradient. However, the variability in stable isotopic signatures along flow path 3 indicate mixing of various source waters along the flow path. Kwicklis *et al.* (2005) and Rose *et al.* (2006) noted that a component of isotopically light water from the relatively high-elevation Pahute Mesa, Timber Mountain, or Yucca Mountain areas mixing with local Fortymile Wash groundwater could produce the lighter isotopic signatures downgradient (J-12 Water Well). For Cold Creek Spring, J-12 Water Well, and Water Well 4, $\delta^{13}\text{C}$ and ^{14}C values are average values that include historical data and data collected for this study (Table 3 and Appendix A).

Volcanic-aquifer flow path 4 is a point-to-point flow path from up- to downgradient with no midgradient sampling site available. In reality, there is not a direct flow path from Tippipah Spring to Water Well 4, but Tippipah Spring is used as surrogate for local groundwater recharge upgradient of Frenchman Flat. Water Well 4 is used as a surrogate to represent the water chemistry downgradient in the volcanic aquifer in the Frenchman Flat area. The Water Well 4 chemical suite has been shown by Hershey *et al.* (2005) and Farnham *et al.* (2006) to be composed only of locally recharged water. The two locations selected to represent groundwater flow in the volcanic aquifer have relatively consistent $\delta^{18}\text{O}$ and $\delta^2\text{H}$.

Table 3. Isotopic data for representative groundwater samples for modeled flow paths shown in Figure 7.

	DIC $\delta^{13}\text{C}$ (‰)	DIC ^{14}C (pmc)	$\delta^2\text{H}$ (‰)	$\delta^{18}\text{O}$ (‰)
Spring Mountains (Carbonate Aquifer)				
Flow Path 1				
McFarland Spring	-11.2	78.1	-99.2	-13.7
Cold Creek Spring	-10.0	68.2	-100.3	-13.7
Indian Springs Prison Well #4	-8.0	5.5	-100.9	-13.7
Flow Path 2				
Deer Creek Spring #1	-10.3	95.9	-102.3	-14.0
Echo 4 Well	-10.0	76.6	-100.6	-13.7
Mifflin Well	-8.6	25.0	-103.0	-14.0
NNSS (Volcanic Aquifer)				
Flow Path 3				
UE-19h	-2.6	10.1	-111.0	-14.6
Cottonwood Spring	-14.7	108.9	-89.0	-11.7
UE-29a #2	-12.6	70.8	-92.4	-12.5
J-12 Water Well	-9.8	30.3	-96.9	-13.1
Flow Path 4				
Tippipah Spring	-12.4	92.2	-95.5	-12.6
Water Well 4	-10.9	18.8	-98.7	-12.6

Travel-time Models

Six travel-time estimates were made for each of the flow paths: 1) uncorrected DOC ^{14}C , 2) uncorrected DIC ^{14}C , 3) DIC-corrected DIC ^{14}C , 4) $\delta^{13}\text{C}$ -corrected DIC ^{14}C , 5) NETPATH “Original Data” without carbon isotopic exchange DIC ^{14}C , and 6) NETPATH “Original Data” with carbon isotopic exchange DIC ^{14}C . NETPATH is a computer program that models the net water-rock, mass-balance reactions between upgradient and downgradient water along a hydrologic flow path and/or computes the mixing proportions when there is more than one upgradient water (Plummer *et al.*, 1994). NETPATH also uses Rayleigh distillation calculations to predict carbon isotopic compositions, including ^{14}C , for the downgradient water (Wigley *et al.*, 1978).

Carbon-14 groundwater ages, and travel times, for both DOC and DIC, are calculated using the equation:

$$T = [\ln(A^{14}\text{C}/A_0)/-0.693] * 5730 \quad (1)$$

where, 5,730 (in years) is the half-life of ^{14}C , A_0 is the initial ^{14}C upgradient, and $A^{14}\text{C}$ is the ^{14}C downgradient.

The DIC-correction model and $\delta^{13}\text{C}$ -correction model adjust DIC ^{14}C travel times based upon changes in DIC concentrations and $\delta^{13}\text{C}$ values between upgradient and downgradient sample locations (Clark and Fritz, 1997). Both the DIC-correction model and $\delta^{13}\text{C}$ -correction model use the following equation to calculate travel times:

$$t = (1/\lambda) * [\ln(^{14}\text{C}_{\text{up}} * q\text{DIC} / ^{14}\text{C}_{\text{down}})] \quad (2)$$

where, $q\text{DIC}$ is the dilution factor and λ is the ^{14}C decay constant (1.21×10^{-4} /yrs). The DIC-correction model dilution factor, $q\text{DIC}$, is calculated by:

$$q\text{DIC} = \text{DIC}_{\text{up}}/\text{DIC}_{\text{down}} \quad (3)$$

where, DIC_{up} and DIC_{down} are the DIC concentrations upgradient and downgradient, respectively.

For the $\delta^{13}\text{C}$ -correction model, $q\text{DIC}$ is replaced with $q\delta^{13}\text{C}$ in Equation 2 and the dilution factor $q\delta^{13}\text{C}$ is calculated by:

$$q\delta^{13}\text{C} = (\delta^{13}\text{C}_{\text{down}} - \delta^{13}\text{C}_{\text{calcite}})/(\delta^{13}\text{C}_{\text{up}} - \delta^{13}\text{C}_{\text{calcite}}) \quad (4)$$

where, $\delta^{13}\text{C}_{\text{calcite}}$ is the $\delta^{13}\text{C}$ signature of the aquifer rock, and $\delta^{13}\text{C}_{\text{up}}$ and $\delta^{13}\text{C}_{\text{down}}$ are the $\delta^{13}\text{C}$ signatures upgradient and downgradient, respectively.

NETPATH Modeling Inputs

The NETPATH models were set up to correct the amount of DIC ^{14}C for carbonate mineral dissolution/precipitation reactions, CO_2 gas exchange, and carbon isotopic fractionation using inverse modeling between upgradient (initial) and downgradient (final) waters. The NETPATH input parameters are listed in Appendix B. The NETPATH phases

and constraints were selected based on the known aquifer rock mineralogy along the flow paths. Four phases were used in the Spring Mountain carbonate-aquifer flow-path models: calcite, dolomite, gypsum, and CO₂ gas. Because of the additional mineral phases in the volcanic-aquifer models, four more phases were added including halite (NaCl), silica (SiO₂), and composite clay and feldspar (tmclay and tmglass from Thomas *et al.* [2002] and Farnham *et al.* [2006]). Volcanic-aquifer flow paths do not include dolomite as a phase because dolomite is not present in volcanic rocks and does not precipitate as a secondary mineral.

Each flow path was modeled twice in NETPATH for DIC ¹⁴C, once without calcite isotope exchange and once using isotope exchange. The isotope exchange function was used to calibrate $\delta^{13}\text{C}$ between the calculated and observed final water $\delta^{13}\text{C}$ values by adjusting the amount of calcite isotopic exchange allowed between the initial water and the aquifer rock (primary and secondary calcite). For example, an initially $\delta^{13}\text{C}$ isotopically heavy calcite (more positive $\delta^{13}\text{C}$ value) will exchange ¹³C for ¹²C with an initially light water (more negative $\delta^{13}\text{C}$ value). During this exchange reaction, ¹⁴C in the water also exchanges for ¹²C in calcite, which is devoid of ¹⁴C (0 pmc ¹⁴C in aquifer calcite). This loss of ¹⁴C from the water to the solid phase by isotopic exchange results in a net decrease in the ¹⁴C of the upgradient water or mixture, and therefore, a reduction in the flow-path travel time. In this study, carbon isotopic exchange is assumed to account for losses of DIC ¹⁴C in addition to carbonate reactions, which would include isotope exchange as well as sorption processes.

The $\delta^{13}\text{C}$ values for calcite and soil gas CO₂ are important input parameters in NETPATH models using isotope exchange. Calcite was assigned $\delta^{13}\text{C}$ values of 0.72 permil (‰) for the NNSS volcanic-aquifer flow paths and -1.88 ‰ for the Spring Mountains carbonate-aquifer flow paths (see the Results section). A ¹⁴C of 0 pmc was also assigned to calcite in all the NETPATH models. Soil gas CO₂ was assigned a $\delta^{13}\text{C}$ value of -20 ‰ for the Spring Mountains carbonate-aquifer flow paths and -18 ‰ for the NNSS volcanic-aquifer flow paths based on average soil gas $\delta^{13}\text{C}$ in the Spring and Grapevine mountains from Quade *et al.* (1989); a ¹⁴C of 100 pmc was assigned to soil gas CO₂.

RESULTS

DOC ¹⁴C versus DIC ¹⁴C

Isotopic and chemical data for all samples collected for this study are listed in Appendix A. Dissolved organic carbon ¹⁴C for thirteen recharge area (upgradient) springs and one well ranged from 96.0 to 120.1 pmc with an average value of 106.2 pmc (Appendix A; Table 4). Dissolved organic carbon ¹⁴C for five downgradient wells and three regional springs ranged from 45.8 to 75.2 pmc with an average value of 62.3 pmc (Appendix A; Table 4; Figure 8). The DIC ¹⁴C for thirteen recharge area springs and one well ranged from 72.6 to 108.9 pmc with an average of 93.3 pmc. The DIC ¹⁴C for seven downgradient wells and three regional springs ranged from 0.7 to 30.3 pmc. Linear regression lines are shown for upgradient and downgradient data sets for DIC ¹⁴C and DOC ¹⁴C to highlight the general trend of the different data sets. Both upgradient and downgradient samples plot below a DIC ¹⁴C to DOC ¹⁴C 1:1 line, but there is much greater difference between DIC ¹⁴C and DOC ¹⁴C for the downgradient samples (Figure 8a). However, DOC and DIC ¹⁴C in upgradient samples are also statistically different (p-value = 1.12×10^{-3}).

Table 4. Average DOC ^{14}C and $\delta^{13}\text{C}$ and uncorrected DIC ^{14}C and $\delta^{13}\text{C}$ for up-, mid-, and downgradient samples.

	Avg. ^{14}C (pmc)	Range (pmc)	Stdv. ^{14}C (pmc)	Avg. $\delta^{13}\text{C}$ (‰)	Stdv. ^{13}C (‰)	#Samples
DOC						
Upgradient	106.2	96.0-120.1	6.6	-22.9	1.4	14
Midgradient	80.0	75.1-88.2	5.8	-24.5	1.6	3
Downgradient	62.3	45.8-75.2	10.4	-23.6	2.4	8
Difference (up-down)	43.9			0.7		
DIC						
Upgradient	93.3	72.6-108.9	10.5	-12.9	1.9	14
Midgradient	67.7	64.2-70.8	2.7	-11.5	1.1	3
Downgradient	11.7	0.7-30.3	11.1	-8.2	2.3	10
Difference (up-down)	81.6			-4.7		

Avg. = average

Stdv. = standard deviation

The DIC $\delta^{13}\text{C}$ and ^{14}C in both volcanic and carbonate aquifers become heavier (less negative) and lower, respectively, during flow for up- to downgradient samples (Figure 8b). The DIC $\delta^{13}\text{C}$ increase significantly for up- to downgradient samples ($p\text{-value} = 1.51 \times 10^{-4}$).

There is no statistical difference for DIC ^{14}C values between upgradient volcanic and carbonate samples ($p\text{-value} = 0.58$), but DIC ^{14}C values in downgradient samples are significantly different for the two rock types ($p\text{-value} = 0.03$). Significant differences in DIC $\delta^{13}\text{C}$ between volcanic and carbonate rocks are observed in both up- and downgradient samples ($p\text{-values}$ of 2.15×10^{-3} and 2.63×10^{-2} , respectively). Carbonate samples exhibit greater decreases in DIC ^{14}C and greater increases in $\delta^{13}\text{C}$ than volcanic waters for up- to downgradient samples (Figure 8b), which is expected for water-rock reactions of the respective rock types.

Dissolved organic carbon in downgradient samples has lower ^{14}C than upgradient samples while the $\delta^{13}\text{C}$ is similar (Figure 8c). The DOC $\delta^{13}\text{C}$ fall within the typical range for DOC derived from plants of approximately -30 to -20 ‰ (Clark and Fritz, 1997) and exhibit no consistent trends for up- to downgradient samples ($p\text{-value} = 0.39$). The DOC ^{14}C and $\delta^{13}\text{C}$ between the rock types are not significantly different for up- or downgradient samples.

The DOC concentrations decrease by 86 percent for up- to downgradient samples; an average of 2.4 mg/L for upgradient samples reduces to 0.3 mg/L for downgradient samples (Table 5). However, DIC and total dissolved solids (TDS) concentrations increase by 30 and 57 percent, respectively (Table 5).

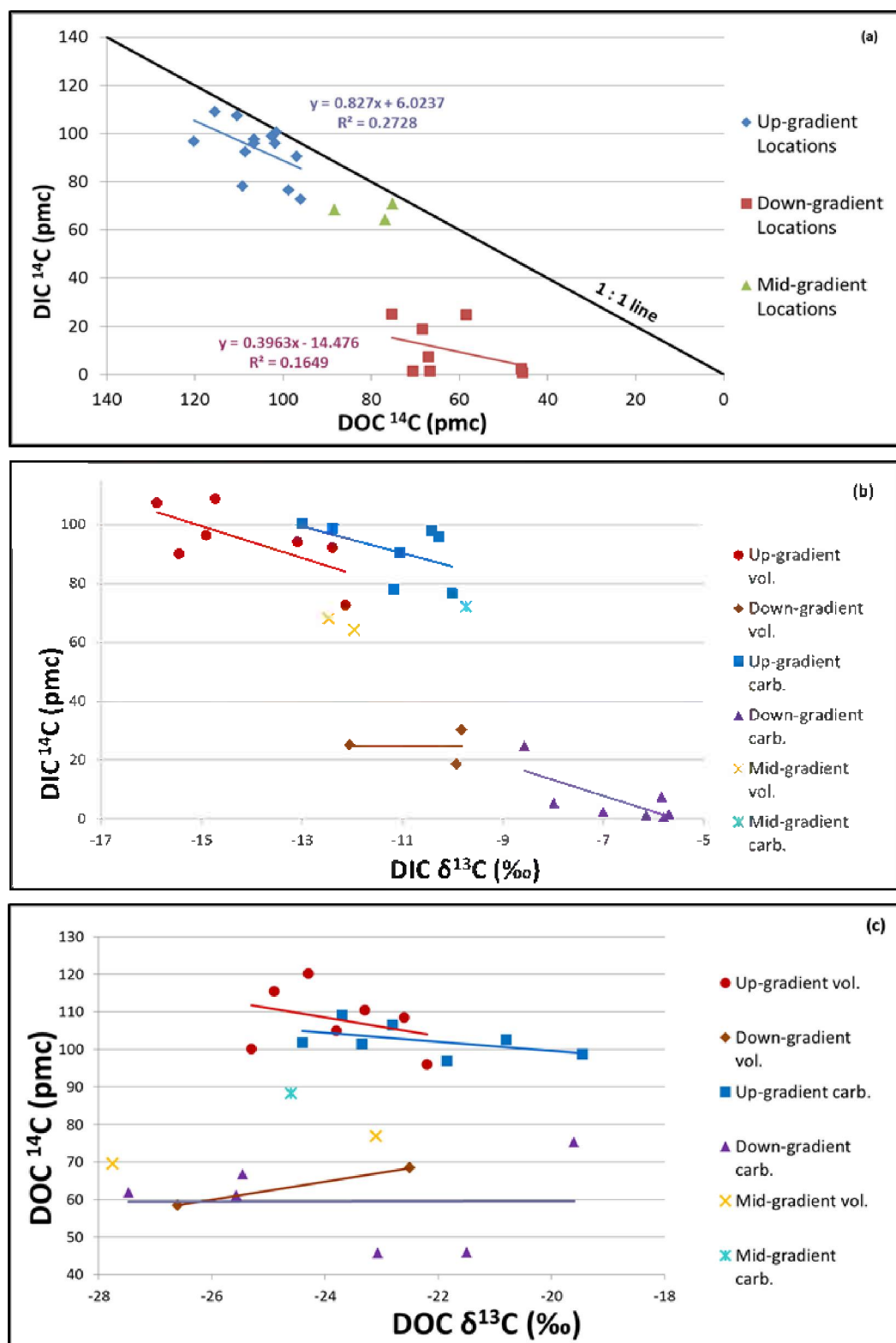


Figure 8. (a) Uncorrected DIC versus DOC ^{14}C by gradient (sample location) with 1:1 line for reference; (b) DIC ^{14}C versus $\delta^{13}\text{C}$ by gradient and rock type (vol. = volcanic and carb. = carbonate); (c) DOC ^{14}C versus $\delta^{13}\text{C}$ by gradient and rock type.

Table 5. Changes in DIC, DOC, and TDS concentrations (in mg/L) for up- to downgradient samples.

	Avg. DIC	Stdv. DIC	Avg. DOC	Stdv. DOC	Avg. TDS	Stdv. TDS
Upgradient	195	118	2.39	1.98	218	80
Downgradient	254	135	0.33	0.17	343	140
% change	30.1 %		-86.1 %		57.2 %	

Avg. = average

Stdv. = standard deviation

DOC ¹⁴C Behavior Experiments

DOC Compound Identification Experiment

Results from the HILIC HPLC analysis show the relative abundances of the DOC compounds eluted over time for a carbonate groundwater flow path in the Spring Mountains from upgradient McFarland Spring and Deer Creek Spring #1 through midgradient Cold Creek Spring to downgradient Indian Springs Prison Well #4 (Figure 9). Except for a series of missing peaks from approximately 16 to 18 seconds in the McFarland Spring sample, all four groundwater spectra show the same general shape over the duration of the HPLC run, which indicates that the DOC compound composition does not change significantly from upgradient to downgradient along this flow path. Although only two upgradient springs were analyzed, the differences between McFarland and Deer Creek Spring #1 may be the result of simple variation between samples or could represent an evolving DOC signature in the groundwater along this flow path.

Unfortunately, even though the LC/MS is capable of detecting organic compounds in the nanomolar range, specific organic compounds could not be identified in these concentrated groundwater samples. Figure 9 shows that there aren't large, single, distinct peaks, rather, there are two clusters of peaks containing a large array of smaller peaks that are close to the same quantity for the groundwater samples. This is as expected for humic substances, which are major constituents of organic substances in soils that, for example, are found in groundwater recharge zones. Humic substances are produced by the biodegradation of dead organic matter and are composed of a complex and heterogeneous mixture of many organic molecules such as plant lignin, polysaccharides, melanin, cutin, proteins, lipids, nucleic acids, and fine char (<http://www.humicsubstances.org/whatarehs.html>, accessed September 15, 2015).

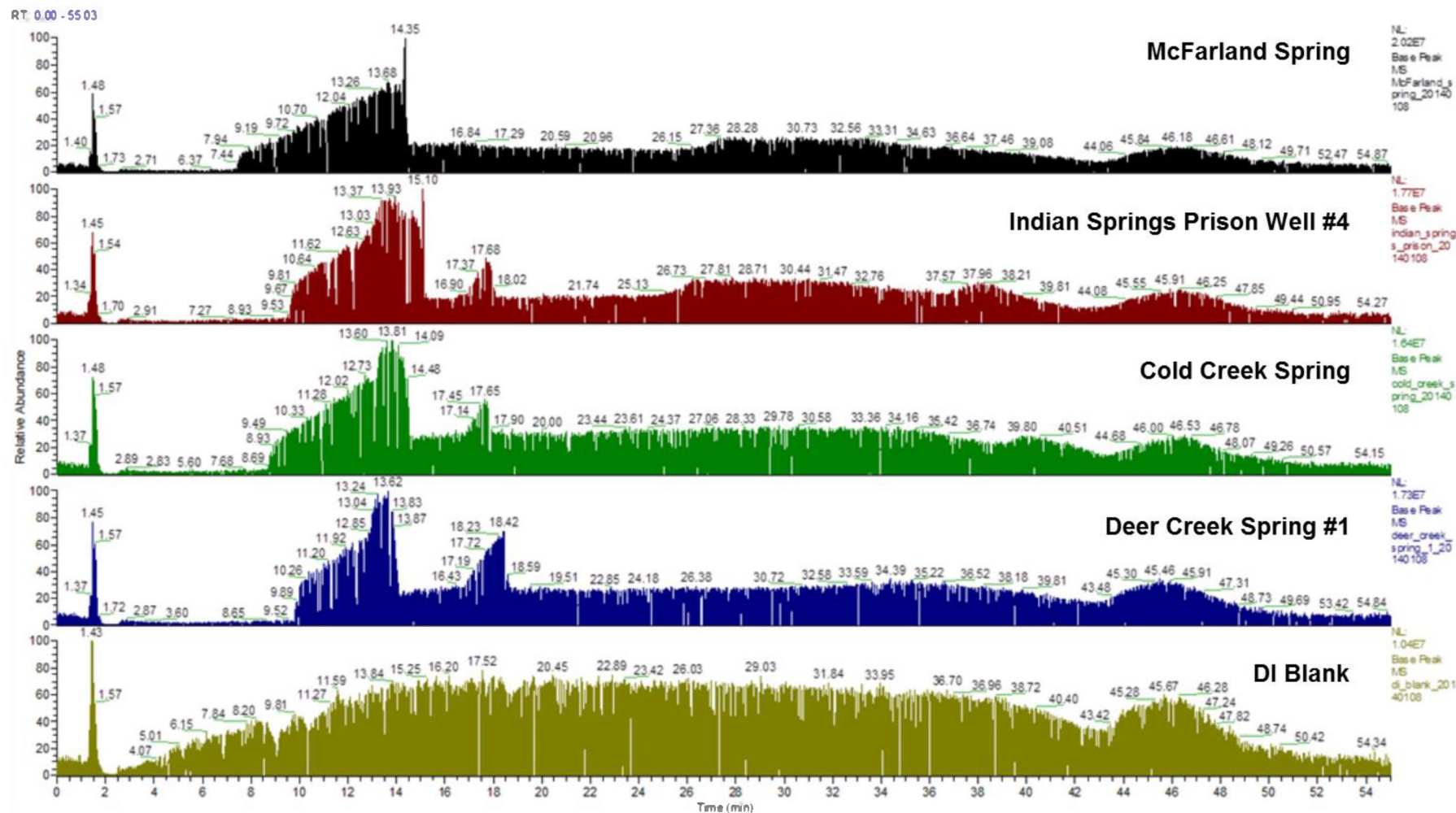


Figure 9. Relative abundances of different molecular-weight DOC compounds in upgradient McFarland Spring and Deer Creek Spring #1, midgradient Cold Creek Spring, and downgradient Indian Springs Prison Well #4. A DI blank is also shown. The time in minutes of the HPLC run is on the x-axis and the relative abundance in percent is on the y-axis. The time of peak elution is shown for each peak for each sample. All data are plotted relative to 100 percent of the highest peak. For example, although the DI water peaks look larger than some of the other sample peaks, the actual concentrations are much lower.

Rock-leaching Experiment

A relatively small amount of organic carbon was leached from the crushed aquifer rock in the batch rock-leaching experiment; 0.40 and 2.28 mg DOC/kilogram (kg) of rock were leached from the carbonate and volcanic rocks, respectively (Table 6). However, the leached DOC was not “dead” as the extant DOC contained 74.6 pmc for the carbonate rocks and 90.7 pmc of ^{14}C for the volcanic rocks (Table 6). Despite removing the outer surface of the rock samples with the goal of excluding any modern organic carbon on the surface of the samples, the high ^{14}C of organic carbon extracted from these rocks is not unexpected. These rocks were collected from outcrops, so they were subjected to surficial processes. Chapelle (1993) has shown that a broad range of aerobic and anaerobic microbes reside on mineral surfaces both in unsaturated (oxic) and saturated zone (anoxic) conditions in rocks. Therefore, because these rocks were collected from surface outcrops, open-system organic carbon has apparently dwarfed any old (“dead”) organic carbon signature in the rocks. Based upon the work of Chapelle (1993) and Chappell and Lovely (1990), it is likely that the extant ^{14}C in the leached DOC came from microbes in the rock samples, which would have modern or nearly modern ^{14}C . It is also possible that some of the ^{14}C is contamination from processing the rocks, but a significant effort was made to minimize contamination from organic carbon during handling and processing of the rocks.

The greater quantity of DOC leached from the volcanic rocks compared to carbonate rocks is also consistent with previous studies that found increased microbial habitation with increased rock and sediment porosities because of the greater surface area available for housing microbes (Chapelle and Lovely, 1990). The greater surface area of the volcanic-rock matrix compared with the carbonate-rock matrix also supports the higher DOC concentrations from the volcanic rock samples associated with microbes, which is consistent with the higher DOC ^{14}C values. The high DOC ^{14}C values also indicate that the amount of DOC from the rock samples is primarily from microbes in the rock samples and not old organic carbon in the rocks, so the amount of old organic carbon present in these rocks that comprise NNSS aquifers is likely low.

Table 6. Average concentration and ^{14}C of DOC leached from crushed carbonate and volcanic outcrop rocks.

	mg DOC/ kg Rock		DOC ^{14}C (pmc)		DOC ^{13}C (‰)		Porosity (%)
	Avg.	Stdv.	Avg.	Stdv.	Avg.	Stdv.	Avg.
Carbonate	0.40	0.02	74.6	6.7	-23.5	1.1	4
Volcanic	2.28	0.38	90.7	2.0	-22.5	0.2	23

Avg. = average

Stdv. = standard deviation

NETPATH Modeling Results

The NETPATH modeling results are presented in Appendix C. One valid model each for the Spring Mountains carbonate-aquifer flow paths 1 and 2 was confirmed by NETPATH. Calcite precipitated while dolomite and gypsum dissolved from upgradient to downgradient in these models. Carbon dioxide both dissolved and exsolved from the groundwater, depending on the model. Carbon isotopic exchange was needed for flow path 1 to obtain modeled $\delta^{13}\text{C}$ values that match the measured $\delta^{13}\text{C}$ value of the final groundwater downgradient in the flow path. The model results for flow path 2 did not need $\delta^{13}\text{C}$ isotopic exchange. The amount of carbon isotopic exchange (in millimoles per kilogram [mmol/kg] of water) needed to obtain measured $\delta^{13}\text{C}$ values is listed in Appendix C.

For the NNSS volcanic-aquifer flow path 3, NETPATH generated five mass-balance models (Appendix C). From the five potential NETPATH models, Model 3 was selected for travel-time estimates since this was the only model of the five that included well UE-29a #2 and had a modeled $\delta^{13}\text{C}$ value consistent with the observed value at J-12 Water Well. Additionally, Model 3 was the only NETPATH model for this flow path that produced $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values similar to the downgradient target water (J-12 Water Well, Table 7). The resulting travel time for this flow path is the difference between the midgradient mixture and the downgradient groundwater (J-12 Water Well).

Table 7. Mixing scenario for NNSS volcanic flow path 3.

Location	Mixing Proportion (%)	DOC ^{14}C (pmc)	DIC ^{14}C (pmc)	$\delta^2\text{H}$ (‰)	$\delta^{18}\text{O}$ (‰)
Upgradient (UE-19h)	28.4	43.0	10.1	-111.0	-14.6
Local Recharge (Cottonwood Spr.)	24.1	115.5	108.9	-89.0	-11.7
Midgradient (UE-29a #2)	47.5	69.6	70.8	-92.4	-12.5
Midgradient Mixture		73.1	62.7	-96.9	-12.9
Downgradient (J-12 Water Well)		68.4	30.3	-96.9	-13.1

For NNSS volcanic-aquifer flow path 4, one valid model for this flow path was generated by NETPATH (Appendix C) except that a small amount of tmclay (0.31 mmol/kg of water) had to dissolve. In reality, clay minerals would instead form by incongruent dissolution of volcanic glass and feldspar minerals along a groundwater flow path. The NETPATH model was also different than the other three flow-path models in that a small amount (0.16 mmol/kg of water) of calcite dissolved. Calcite dissolution is expected along this flow path because upgradient recharge water (surrogate Tippipah Spring) is undersaturated with respect to calcite. Carbon isotopic exchange was needed for flow path 4 to obtain modeled $\delta^{13}\text{C}$ values that match the measured $\delta^{13}\text{C}$ value of the downgradient groundwater (surrogate Water Well 4). The match in the DIC $\delta^{13}\text{C}$ between modeled and observed compositions and the consistency of the stable isotopes $\delta^2\text{H}$ and $\delta^{18}\text{O}$ (Table 3) supports the previous observation that local recharge is the source water of downgradient groundwater in the volcanic aquifer in Frenchman Flat (Water Well 4; Farnham *et al.*, 2006; Hershey *et al.*, 2005).

The assignment of calcite $\delta^{13}\text{C}$ values in NETPATH models was based on previously established values (Table 8). The calcite $\delta^{13}\text{C}$ values for isotopic exchange used by Thomas *et al.* (1996) and Morse (2002) were a mixture of primary and secondary calcite $\delta^{13}\text{C}$ values. Thomas *et al.* (1996) assumed a mixture of 50 percent primary ($\delta^{13}\text{C} = 1.2\text{‰}$) with 50 percent secondary ($\delta^{13}\text{C} = -3.75\text{‰}$) calcite. Morse (2002) assumed a mixture of 37 percent primary ($\delta^{13}\text{C} = 1.2\text{‰}$) with 63 percent secondary ($\delta^{13}\text{C} = -4.7\text{‰}$) calcite. For both studies, the isotopic value of the secondary calcite was calculated from the known $\delta^{13}\text{C}$ of the groundwater in the flow path. The Spring Mountains flow-path models in this study did not differentiate between secondary and primary calcite for isotopic exchange. Instead, a single $\delta^{13}\text{C}$ of -1.88‰ (and DIC ^{14}C of 0 pmc) was used, which was an average of the values used by Thomas *et al.* (1996) and Morse (2002). The $\delta^{13}\text{C}$ analysis of NNSS and Oasis Valley volcanic-rock core (Rose *et al.*, 1999; Benedict *et al.*, 2000) yielded a 0.72‰ average value for secondary calcite (Table 8). The NETPATH isotope exchange reactions for NNSS flow paths, which are entirely within volcanic rock, used this secondary calcite $\delta^{13}\text{C}$ value and a ^{14}C of 0 pmc.

Table 8. Average primary and secondary calcite $\delta^{13}\text{C}$ values for southern Nevada carbonate and volcanic rocks.

Calcite Isotopic Compositions	Secondary Calcite		Primary Calcite	
	$\delta^{13}\text{C}$ (‰)	# samples	$\delta^{13}\text{C}$ (‰)	# samples
Secondary calcite from Pahute Mesa-Oasis Valley volcanic rocks (Rose <i>et al.</i> , 1999; Benedict <i>et al.</i> , 2000)	0.72	33	nd	nd
Thomas <i>et al.</i> (1996) calculated Spring Mountains calcite (50% secondary, 50% primary)	-3.75	nd	1.2	nd
Morse (2002) calculated Spring Mountains calcite (63% secondary, 39% primary)	-4.7	nd	1.2	nd

nd = no data

DISCUSSION

DOC ^{14}C A_0

The consistency of ≥ 100 pmc DOC ^{14}C in recharge areas indicates that the upgradient sample locations selected are representative of modern recharge. Only two of the fourteen upgradient sample locations, Mormon Well Spring (96.9 pmc) and Cane Spring (96.0 pmc), had DOC ^{14}C slightly less than 100 pmc. Previously, the lack of measured DOC ^{14}C in recharge areas required the use of uncertain DOC ^{14}C A_0 values, which resulted in considerable uncertainty in downgradient groundwater ages and flow-path travel times. Verification of modern DOC ^{14}C in recharge areas decreases the uncertainty in DOC ^{14}C A_0 values and corresponding groundwater ages and travel times using the DOC ^{14}C groundwater dating method.

There are two locations where measurable tritium suggests recent recharge, but DOC ^{14}C is less than 100 pmc; Cold Creek Spring (88.2 pmc) and well UE-29a #2 (75.1 pmc). Tritium is an indicator of young water (less than approximately 60 years) since tritium has a half-life of approximately 12.5 years and an atmospheric spike was produced from above-ground nuclear testing. Older waters have no detectable tritium because either all of the initial tritium has decayed and/or the water was recharged prior to above-ground nuclear testing. The less than 100 pmc DOC ^{14}C and measurable tritium at these two locations may result from mixing of infiltrating groundwater (100 pmc or higher) near the spring or well with older groundwater (<100 pmc), dissolution of older sedimentary organic material as the water infiltrates prior to becoming isolated in a closed system, and/or dissolution of older sedimentary organic material as the water flows through alluvial deposits that contain older sedimentary organic matter (SOM). Because of their relative position slightly downgradient from known recharge areas, the presence of measureable tritium, and elevated, but less than 100 pmc, these sample locations are categorized as midgradient along their respective flow paths. Tramp Spring in the Kawich Range is also slightly downgradient from known recharge areas and has less than 100 pmc (DOC ^{14}C = 76.8 pmc); however, there are no tritium data available for Tramp Spring (UGTA, 2008).

Decrease in DOC Concentrations from Recharge to Downgradient Areas

The increase in DIC and TDS during groundwater flow (Table 5) indicates that the volcanic and carbonate aquifers examined are closed systems after groundwater leaves the recharge areas because water-rock reactions, rather than external inputs, control changing water chemistry. After isolation from recharge areas into closed-system conditions, on average, 86 percent of DOC in upgradient recharge areas is lost during groundwater flow to downgradient areas of the flow systems (Table 5). This loss of DOC as groundwater flows to downgradient areas could occur because of microbial degradation.

Microbially mediated DOC oxidation to CO_2 is a likely explanation for the observed DOC reduction from up- to downgradient locations. Chapelle (1993) noted that DOC decreases and corresponding DIC increases are commonly associated with bacterial degradation in both saturated- and unsaturated-zone conditions. Winograd *et al.* (1982) demonstrated that there is 2 to 8 mg/L of dissolved oxygen in deep carbonate aquifers in southern Nevada. This oxygen could provide a source for bacterial respiration and oxidation of DOC to CO_2 . Furthermore, it has been demonstrated that microbial activity in deep, anoxic aquifers is widespread because anaerobic bacteria and facultative anaerobes can persist by using nitrate, sulfate, iron, magnesium, phosphate, or other inorganic components as electron acceptors to produce compounds that are subsequently used by aerobic bacteria in oxic zones (Moncure *et al.*, 1981; Purdy *et al.*, 1992; Lovely and Chapelle, 1995). Godsy (1980) and Dockins *et al.* (1980) have shown that deep wells tapping regional flow systems ubiquitously contain bacteria and Pederson and Ekendahl (1990) likewise observed concentrations of more than 10⁵ bacteria cells/mL in deep regional aquifers. These bacteria use both chemical and DOC constituents for electron acceptors and frequently work symbiotically to oxidize DOC to CO_2 , which is the case with aerobes and fermenters (Chapelle, 1993). Although the total amount of bacterial oxidation declines rapidly with reductions in dissolved oxygen, the limiting factor in microbial activity is the availability of carbon sources for aerobic bacteria and not the dissolved oxygen content of the water (Chapelle, 1993). Therefore, bacteria in both unsaturated and saturated-zone settings in southern Nevada aquifers could effectively reduce DOC concentrations.

Although microbes likely play a role in DOC concentration reductions along flow paths in southern Nevada, other processes could also reduce DOC concentrations. Adsorption, matrix diffusion, or simple dispersion could also reduce DOC concentrations along flow paths in the study area. However, adsorption and/or matrix diffusion of DOC has been shown to be small in southern Nevada aquifers over the short time frame of laboratory experiments (Hershey *et al.*, 2016). A reduction in DOC concentration along a flow path does not preclude the use of DOC as a conservative dating tool as long as no process causes significant DOC ^{14}C fractionation along the flow path and no old organic carbon is added to the water from aquifer rocks. An increase in DOC $\delta^{13}\text{C}$ values would occur if bacterial fractionation is a significant process (Clark and Fritz, 1997). However, average DOC $\delta^{13}\text{C}$ values in up- and downgradient locations are -23.1 and -25.0 ‰, respectively, which shows a slight decrease rather than increase from upgradient to downgradient groundwater. The insignificant (not statistically significant) change in DOC $\delta^{13}\text{C}$ from up- to downgradient locations suggests that carbon isotopic fractionation is not occurring and that variations are more likely a result of differing recharge water DOC $\delta^{13}\text{C}$ values and routine analytical variation. The DOC rock-leaching experiments also showed that little old DOC is likely to leach from southern Nevada aquifer rocks.

Evaluation of DOC ^{14}C Laboratory Experimental Results

Changes in DOC concentrations and compounds along flow paths and the potential effect of those changes on DOC ^{14}C were examined in laboratory experiments to identify DOC compounds, leaching experiments to quantify DOC from aquifer rocks, and experiments to quantify matrix-diffusion coefficients for DOC ^{14}C . The implications of the DOC compound identification and rock-leaching experimental results on DOC ^{14}C transport are discussed below. The DOC ^{14}C matrix-diffusion results are discussed in Hershey *et al.* (2016).

DOC Compound Identification

Groundwater spectra for the two recharge area springs and a downgradient spring and a downgradient well show the same general shape over the duration of the HPLC run (Figure 9), which suggests that the DOC compound composition does not change significantly from upgradient to downgradient groundwater along this carbonate-aquifer flow path. Although DOC concentration decreases from recharge-area to downgradient groundwater, the organic compounds are the similar, indicating that DOC ^{14}C is unaffected by other processes in the aquifers such as microbial degradation.

Rock Leaching

The small amount of DOC leached from the high surface area of the crushed rocks (Table 6), and more importantly, the high DOC ^{14}C (90.7 and 74.6 pmc) of the leachate, suggest that most of the leached DOC was from young microbes in the rock outcrops samples. These results support the hypothesis that DOC ^{14}C dilution by old organic carbon (kerogen) in volcanic and carbonate aquifer rocks is minimal. Also, the results of the leaching experiments are consistent with the DOC compound identification experimental results in that any old organic compounds leached from the aquifer rocks that are millions to hundreds of millions years old would likely consist of different organic compounds than those found in modern day recharge area soils.

Evaluation of Laboratory Experimental Results on DOC ^{14}C Transport

Four primary lines of evidence suggest that DOC ^{14}C behaves conservatively in southern Nevada aquifers, and therefore, using DOC ^{14}C to date groundwater is a valid method. First, the loss of DOC from up- to downgradient groundwater implies that organic carbon is removed from, rather than added to, groundwater during flow. Second, because only small quantities of DOC were leached from aquifer rock experiments, and the leached DOC had high ^{14}C indicating that most of the DOC was from microbes on the rock outcrop samples and not old organic carbon in the rocks, the dilution of DOC ^{14}C in groundwater from dissolution of aquifer organic carbon is likely minimal. Third, DOC compounds in recharge area upgradient groundwater and in downgradient groundwater appear to be the same as shown in HILIC HPLC spectra (Figure 9). Fourth, the DOC ^{14}C matrix diffusion coefficients measured in laboratory experiments are lower than for DIC ^{14}C , mostly because of the large size of DOC (Hershey *et al.*, 2016). The greater diffusion of DIC ^{14}C relative to DOC ^{14}C would produce older groundwater ages using DIC ^{14}C than DOC ^{14}C , which is consistent with previous observations.

The results of the leaching experiments support the overall paucity of organics in southern Nevada carbonate and volcanic aquifers. Additionally, Artinger *et al.* (1996) demonstrated that SOM dissolution typically results in elevated DOC concentrations ($> 10 \text{ mg/L}$), whereas, groundwater with low DOC ($\leq 3 \text{ mg/L}$) contained little dissolved SOM. The DOC concentrations in groundwater in this study are quite low (generally $< 1\text{-}2 \text{ mg/L}$) and decline significantly from up- to downgradient locations, which further indicates that SOM dilution, which can cause elevated DOC concentrations, is not occurring. The high DOC ^{14}C of the leached DOC from the outcrop-rock-leaching experiment implies that modern surficial DOC may exist in unsaturated zones, but that aquifer rocks have relatively little organic carbon.

The SOM dilution of humic acid ^{14}C typically occurs only in deposits rich in SOM such as oil shales, clayey or organic-rich sandstones, and marly limestones (Artinger *et al.*, 1996). Carbonate rocks typically contain SOM in the form of alkanes rather than the aromatic fulvic-acid-like compounds (Frye *et al.*, 1993). Particulate organic matter concentrations even in deep, sandy aquifers are known to be very low (≤ 0.1 percent) compared with clay layers, which can be organic-rich and highly variable (1-50 percent) (McMahon *et al.*, 1990; Johnson and Wood, 1993; Lovely and Chapelle, 1995). Volcanic rocks of the NNSS are primarily ash-fall and ash-flow tuffs. The extremely high formative temperatures of these rocks would vaporize nearly all entrained organic matter (Moncure *et al.*, 1981). The carbonate rocks, which have very low porosities, leached even less DOC in the experiments than the volcanic rocks. Therefore, one would not expect significant SOM to exist in the organic-poor volcanic tuff and carbonate rocks that comprise the hydrostratigraphic units of the NNSS and Spring Mountains area aquifers.

The observed loss of DOC in groundwater during flow could be a result of bacterial oxidation of DOC to CO_2 , natural DOC degradation, sorption (of less soluble compounds), or simple dispersion. It is unknown whether bacterially mediated carbon isotopic fractionation, if it is occurring, significantly affects the amount of DOC ^{14}C in downgradient aquifers. The overall low DOC ^{14}C diffusion coefficients and the low DOC diffusion compared to bromide diffusion coefficients in laboratory matrix diffusion experiments indicate that loss of DOC ^{14}C by matrix diffusion is less than for DIC ^{14}C (Hershey *et al.*, 2016). Purdy *et al.* (1992),

Artinger *et al.* (1996), and Drever (1997) have shown that DOC sorption onto aquifer rocks is negligible because old groundwater would have long since reached equilibrium between mineral surfaces and DOC in aquifer rocks.

DOC ^{14}C versus DIC ^{14}C Ages

Although the amount of ^{14}C is high, as expected, in upgradient recharge areas for both DIC and DOC, the amount of DOC ^{14}C is higher than DIC ^{14}C (Figure 8). This difference is pertinent to the A_0 value chosen to calculate ages. This difference also implies that DIC ^{14}C dilution is occurring even within the relatively short flow paths from recharge infiltration to upgradient groundwater. This difference results from infiltrating water dissolving calcite and dolomite in carbonate rock and unconsolidated sediments, and dissolving or precipitating unsaturated-zone pedogenic carbonate.

The difference between DIC ^{14}C and DOC ^{14}C increases as groundwater flows along a flow path as more water-rock reactions occur, producing downgradient waters with even lower DIC ^{14}C than DOC ^{14}C (Figure 8a-c). As a result, DIC ^{14}C in downgradient waters in the study area are, on average, 52 pmc lower than DOC ^{14}C (Appendix A). This difference in pmc results in a difference ranging from 5,500 to 15,500 years for uncorrected DIC ^{14}C travel times (Equation 1 compared with DIC ^{14}C travel times in downgradient groundwater in Appendix C). The DIC ^{14}C and DOC ^{14}C calculated groundwater ages are both maximum ages because any potential carbonate mineral dissolution, matrix diffusion, adsorption, isotope exchange, or addition of old organic carbon from aquifers would result in lower DIC ^{14}C or DOC ^{14}C .

The lower DIC ^{14}C than DOC ^{14}C illustrates the effect of DIC ^{14}C dilution from carbonate-rock reactions (calcite and dolomite dissolution and precipitation and the associated isotopic fractionation during these processes). Primary carbonate rock has relatively heavy DIC $\delta^{13}\text{C}$ (approximately 0 ‰) compared to soil zone CO_2 gas ($\delta^{13}\text{C}$ ranging from approximately -30 to -10 ‰). As a result, carbonate-mineral dissolution isotopically enriches (value becomes less negative) the $\delta^{13}\text{C}$ of the groundwater (Clark and Fritz, 1997). Dissolved inorganic carbon $\delta^{13}\text{C}$ enrichment occurs as an initially light (more negative) DIC $\delta^{13}\text{C}$ in upgradient recharge area groundwater, that derived its initial DIC $\delta^{13}\text{C}$ value from soil zone CO_2 gas dissolution in open-system conditions, evolves to an isotopically heavier (less negative) DIC $\delta^{13}\text{C}$ value downgradient under closed-system conditions.

The effect of carbonate-mineral reactions on decreasing DIC ^{14}C is also illustrated by there being no statistical difference between upgradient volcanic and carbonate groundwater DIC ^{14}C , but significantly lower DIC ^{14}C in downgradient groundwater in carbonate-rock aquifers than in volcanic-rock aquifers. The effect of carbonate-mineral reactions is also observed in the heavier DIC $\delta^{13}\text{C}$ of groundwater in carbonate-rock aquifers than in volcanic-rock aquifers (Figure 8). Less DIC ^{14}C dilution occurs in volcanic-rock aquifers than in carbonate-rock aquifers because there is less carbonate material in volcanic aquifer systems than carbonate aquifer systems. Because of the sensitivity to aquifer mineralogy, water-rock reactions in carbonate-rock aquifers require more DIC ^{14}C groundwater age correction than groundwater in volcanic-rock aquifers.

Other processes such as matrix diffusion, isotope exchange, or sorption can also play a role in decreasing groundwater DIC ^{14}C . Because DOC ^{14}C behaves more conservatively than DIC ^{14}C in these settings, it can be assumed that such processes also increase DIC ^{14}C

groundwater ages relative to DOC ^{14}C ages, which is consistent with the observed lower DIC ^{14}C than DOC ^{14}C in these aquifers. Mass-balance models, such as NETPATH and PHREEQC, are used to correct for changes in DIC ^{14}C from these processes. However, because these processes are highly variable and hard to quantify in natural groundwater systems, various water-rock reaction, mass-balance models often yield large inconsistencies in DIC age corrections (Clark and Fritz, 1997).

Modeled Flow-path Travel Times

Based on the results and observations from this study discussed previously, DOC ^{14}C ages and travel times do not require any corrections. Various correction models were applied to DIC ^{14}C ages to correct for water-rock reactions along the flow paths. Figure 10 and Table 9 compare the various travel-time calculations (DOC ^{14}C , uncorrected DIC ^{14}C , DIC-corrected DIC ^{14}C , $\delta^{13}\text{C}$ -corrected DIC ^{14}C , and NETPATH water-rock reaction corrected [with and without carbon isotopic exchange]) for each of the four flow paths including the up- to midgradient and mid- to downgradient flow paths for the two carbonate-aquifer flow paths (referred to as upper and lower in Figure 10) and for the up- to downgradient volcanic-aquifer flow paths 3 and 4.

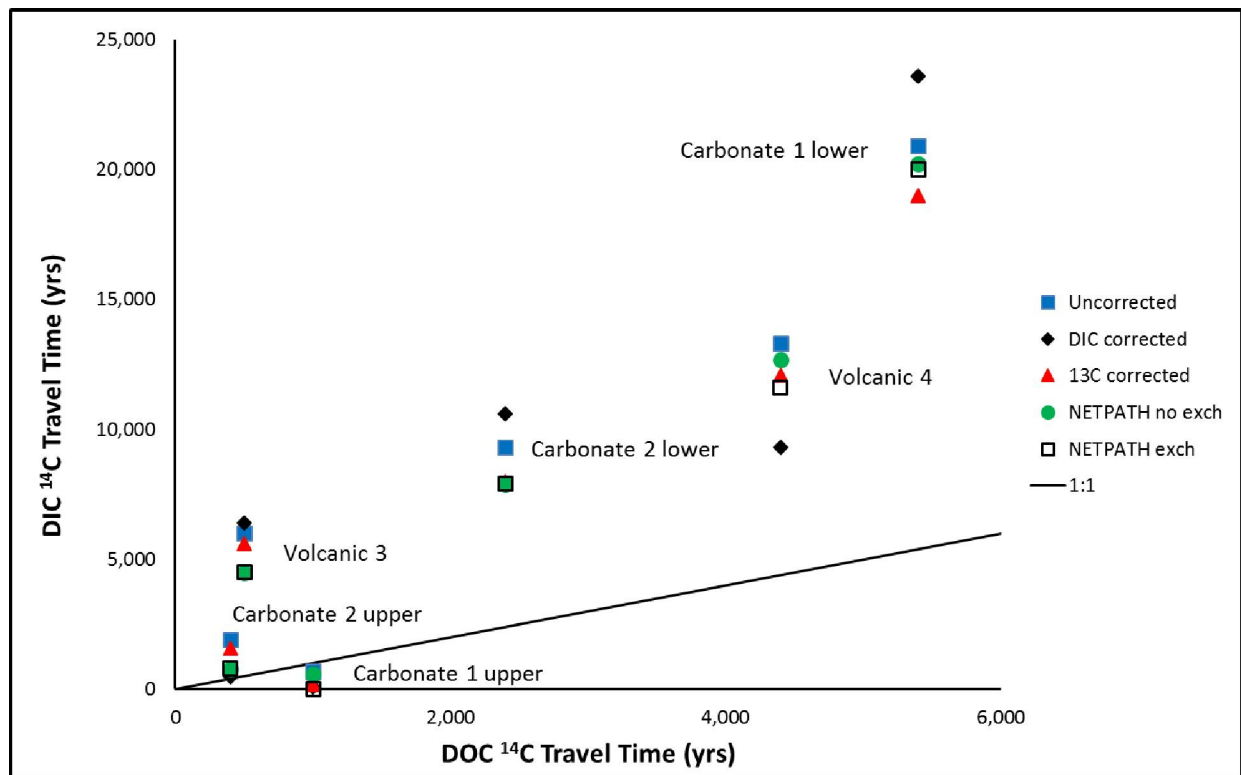


Figure 10. DOC ^{14}C travel times compared to uncorrected DIC ^{14}C , DIC corrected DIC ^{14}C , $\delta^{13}\text{C}$ corrected DIC ^{14}C , and NETPATH corrected (with and without carbon isotopic exchange) travel times with 1:1 line for flow paths 1-4.

Table 9. Comparison of flow-path travel time calculations, in years, for flow paths 1-4. Travel times are rounded to the nearest hundred years.

	DOC ¹⁴ C	DIC ¹⁴ C Uncorrected	DIC ¹⁴ C DIC-corrected	DIC ¹⁴ C $\delta^{13}\text{C}$ -corrected	DIC ¹⁴ C NETPATH (no carbon isotopic exchange)	DIC ¹⁴ C NETPATH (carbon isotopic exchange)
Spring Mountains (carbonate)						
<u>Flow Path 1</u>						
Upgradient to midgradient	1,000	700	100	200	600	modern
Midgradient to downgradient	5,400	20,900	20,900	19,000	20,200	20,000
<u>Flow Path 2</u>						
Upgradient to midgradient	400	1,900	500	1,600	800	800
Midgradient to downgradient	2,400	9,300	9,300	8,000	7,900	7,900
NNSS (volcanic)						
<u>Flow Path 3</u>						
Upgradient to downgradient	500	6,000	6,000	5,600	4,500	4,500
<u>Flow Path 4</u>						
Upgradient to downgradient	4,400	13,300	9,300	12,100	12,700	11,600

DOC ^{14}C Travel Times

The DOC ^{14}C travel times in this study are hundreds to thousands of years shorter than uncorrected and corrected DIC ^{14}C travel times for the four main flow paths (Figure 10; Table 9) except for the up- to midgradient portion of carbonate-aquifer flow path 1. The shortest carbonate-aquifer DOC ^{14}C travel time is 400 years in flow path 2 from upgradient (Deer Creek Spring #1) to midgradient (Echo 4 Well) while the longest DOC ^{14}C travel time in the carbonate-aquifer is 5,400 years in flow path 1 from midgradient (Cold Creek Spring) to downgradient (Indian Springs Prison Well #4). The two volcanic-rock-aquifer flow paths produced DOC ^{14}C groundwater travel times of 500 years for flow path 3 and 4,400 years for flow path 4.

Uncorrected DIC ^{14}C Travel Times

Uncorrected DIC ^{14}C flow-path travel times are thousands of years longer than DOC ^{14}C travel times and clearly overestimate flow-path travel times except for the up-to midgradient portion of carbonate-aquifer flow path 1. The difference between uncorrected DIC ^{14}C and DOC ^{14}C travel times is greatest in the carbonate-aquifer flow paths (Figure 10; Table 9). This is because of the greater amount of carbonate minerals in the carbonate aquifers as opposed to the volcanic aquifers, which only contain calcite in minor amounts as a secondary mineral.

DIC-Corrected and $\delta^{13}\text{C}$ -Corrected DIC ^{14}C Travel Times

The DIC-correction model corrects DIC ^{14}C for net additions in DIC from dissolution of carbonate containing materials (calcite, dolomite, and CO_2) along the flow path. Three of the flow paths have shorter DIC ^{14}C travel times because of the DIC-correction model, carbonate-aquifer flow paths 1 and 2 from up- to midgradient and volcanic flow path 4, while the other three flow-path travel times are unchanged. Travel times decreased from 600 to 4,000 yrs depending on the flow path; the greatest change in travel time (4,000 yrs) was for volcanic-aquifer flow path 4. Since there are no primary carbonate minerals (calcite and dolomite) along this flow path, the addition of DIC was likely from dissolution of additional CO_2 gas from the soil zone in the upper portion of the flow path.

There was no change in DIC ^{14}C travel times for three flow paths because DIC decreased along the flow paths. In the two carbonate-aquifer flow paths, calcite saturation is reached quickly, calcium and DIC is added to groundwater by dissolution of dolomite, and more calcium is added by gypsum dissolution. The excess calcium and DIC is removed from the groundwater by precipitation of calcite. Because there is even more calcium added to groundwater from gypsum dissolution, calcite precipitation removes more DIC from the groundwater resulting in a net decrease in DIC along the flow path. The DIC-correction model only corrects DIC ^{14}C ages for net additions of DIC. For volcanic-aquifer flow path 3, calcium is added to groundwater by dissolution of calcium containing volcanic glass and feldspars. Assuming an aquifer system closed to any soil gas reservoir, no CO_2 , and therefore, no additional DIC would be added to the groundwater along the flow path. Excess calcium from volcanic glass and feldspar dissolution precipitates as secondary calcite removing DIC from the groundwater along the flow path.

The $\delta^{13}\text{C}$ -correction model corrects DIC ^{14}C for changes in $\delta^{13}\text{C}$ from dissolution of calcite and the net change in $\delta^{13}\text{C}$ along the flow path by processes other than calcite dissolution. The $\delta^{13}\text{C}$ -correction model reduced DIC ^{14}C travel times for all flow paths from 300 to 1,300 years. For volcanic-aquifer flow paths, since primary carbonate minerals are not present in the flow system, the decrease in travel times because of the increases in $\delta^{13}\text{C}$ along the flow path must be from other isotopic processes such as isotopic exchange with secondary calcite in fracture linings in the aquifer.

NETPATH Modeled DIC ^{14}C Travel Times

The geochemical model NETPATH accounts for carbonate mineral and CO_2 gas reactions through mass-balance calculations and the carbon-isotopic fractionation associated with these reactions. The model also considers reactions of calcium- and magnesium-containing minerals (gypsum, tmglass, and tmclay) that affect calcite dissolution and precipitation and dolomite dissolution. Other processes such as isotopic exchange/sorption are also corrected for in NETPATH by the use of the “isotope exchange” function when it is applied.

The NETPATH models with no carbon isotopic exchange decreased DIC ^{14}C travel times from uncorrected DIC ^{14}C travel times in all six flow paths. Travel times decreased by 100 to 1,500 yrs depending on the flow path. NETPATH models with no carbon isotopic exchange decreased DIC ^{14}C travel times from DIC- and $\delta^{13}\text{C}$ -corrected DIC ^{14}C travel times in half of the flow paths by 100 to 1,500 years and increased travel times in the other half of by 300 to 3,400 yrs. There was no pattern in which flow paths were shorter or longer or by correction method. NETPATH models with no carbon isotopic exchange travel times were still substantially longer than all but one DOC ^{14}C travel time (Table 9).

The NETPATH models with carbon isotopic exchange decreased DIC ^{14}C travel times from uncorrected DIC ^{14}C travel times in all six flow paths. Travel times decrease by 700 to 1,700 yrs depending on the flow path. NETPATH models with carbon isotopic exchange decreased DIC ^{14}C travel times from DIC- and $\delta^{13}\text{C}$ -corrected DIC ^{14}C travel times in most of the flow paths by 100 to 1,500 years and increased travel times in three other flow paths by 100 to 2,300 yrs. NETPATH models with carbon isotopic exchange travel times were still substantially longer than all but one DOC ^{14}C travel time (Table 9).

The changes in DIC ^{14}C travel times for the NETPATH models did not correlate with aquifer rock type, even though one would expect the models to reduce travel times more along carbonate aquifer flow paths where more carbonate mineral reactions occur. The greatest decrease occurred along flow path 3 (1,500 yrs) despite the paucity of carbonate minerals in this flow path. This suggests that all reactions and/or mixing waters are not fully represented in the model. Questionable chemical feasibility for this flow path is also indicated by the ignored precipitation constraint for tmclay (Appendix D), which may suggest another source water(s) with a different water chemistry or different chemical compositions of the composite glass and/or clay. Also, as described above, recent work on water-level contours indicate that this may not be an actual groundwater flow path.

The NETPATH models mostly yielded the shortest DIC ^{14}C travel times, but these were still hundreds to thousands of years longer than DOC ^{14}C travel times (excluding flow path 1 up- to midgradient). The NETPATH models, which correct for water-rock reactions, likely overestimate travel times because processes other than carbonate reactions such as

matrix diffusion and/or isotope exchange may be causing additional dilution of DIC ^{14}C , and therefore, additional increases in DIC ^{14}C travel times. The NETPATH model with carbon-isotopic exchange is designed to correct for some of these processes. However, it apparently does not capture all of the additional dilution of DIC ^{14}C occurring along the flow paths. Additionally, DIC ^{14}C travel times vary greatly depending on the correction model.

CONCLUSIONS

Results from this study support the DOC ^{14}C groundwater dating technique as a viable method for estimating groundwater ages in low-DOC groundwater. This approach provides an additional tool that can be compared to the traditional method of dating groundwater with DIC ^{14}C , which requires complex corrections that do not always capture all of the changes in groundwater DIC ^{14}C along a flow path. The DOC ^{14}C groundwater dating method is valid in closed-system, low-porosity aquifers dominated by fracture-flow that are devoid of significant organic matter, conditions often found in southern Nevada. In such aquifers, corrections for gain or loss of DOC ^{14}C by processes other than radiocarbon decay are minor because little, or no, organic carbon enters the groundwater and adsorption of DOC to aquifer mineral surfaces is minimal.

In this study, DOC ^{14}C groundwater ages were hundreds to thousands of years lower than uncorrected and corrected DIC ^{14}C ages. Dissolved organic carbon ^{14}C ages ranged from 400 to 5,400 years as compared to DIC ^{14}C ages that ranged from modern to 20,900 years. These large differences in groundwater ages also result in large differences in travel times. The DIC ^{14}C groundwater ages are greatly influenced by carbonate mineral and CO_2 gas dissolution/precipitation/exsolution reactions and other unquantified water-rock reactions, such as matrix diffusion, isotope exchange, or adsorption, which are not always adequately accounted for in DIC ^{14}C groundwater age correction models.

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APPENDIX A: DATE SAMPLED, SAMPLE LOCATION, SITE ELEVATION, AREA SAMPLE IS FROM, ROCK TYPE THE WELL OR SPRING IS LOCATED IN, CHEMICAL, AND ISOTOPIC DATA FOR ALL GROUNDWATERS SAMPLED.

Table A-1. Sample type and location.

WGA83/NAD84 (dms)						
	Sample Date	Latitude	Longitude	Elevations (ft)	Area	Rock Type
Upgradient locations						
John's Spring	2/23/2011	37 14 49.9	116 04 27.5	5,821	Area 15 NNSS	volcanic
White Rock East Spring	2/24/2011	37 12 05.7	116 07 53.4	4,838	Area 12 NNSS	volcanic
Wamp Spring	2/9/2011	36 38 30.7	115 04 11.2	5,479	Sheep Range	carbonate
Mormon Well Spring	2/10/2011	36 38 39.1	115 05 47.2	6,440	Sheep Range	carbonate
Captain Jack Spring	2/28/2011	37 10 06.8	116 10 06.9	5,723	Area 12 NNSS	volcanic
Cottonwood Spring	3/16/2011	36 53 52.9	116 23 34.4	4,196	Area 25 NNSS	volcanic
Tippipah Spring	2/28/2011	37 02 34.9	116 12 11.6	5,161	Area 16 NNSS	volcanic
Cane Spring	3/1/2011	36 47 55.6	116 05 42.1	4,072	Area 27 NNSS	volcanic
Deer Creek Spring #2	3/19/2011	36 18 26.7	115 37 41.4	8,640	Spring Mountains	carbonate
Deer Creek Spring #1	3/18/2011	36 18 15.0	115 38 21.0	9,330	Spring Mountains	carbonate
McFarland Spring	3/24/2011	36 22 54.7	115 44 38.0	7,709	Spring Mountains	carbonate
Unnamed Spring East Kawich Spring	6/23/2011	37 56 40.0	116 21 50.0	6,502	Kawich Range	volcanic
Upper Mack's Canyon Spring	8/3/2011	36 20 07.0	115 41 11.0	8,891	Spring Mountains	carbonate
Echo 4 Well	10/18/2011	36 26 69.0	115 66 15.1	7,822	Spring Mountains	carbonate
Midgradient Location						
Cold Creek Spring	2/22/2011	36 24 41.3	115 44 37.7	6,323	Spring Mountains	carbonate
Tramp Spring	6/23/2011	37 53 26.5	116 22 09.3	7,192	Kawich Range	volcanic
UE-29a #2	12/13/2011	36 56 28.7	116 22 26.0	3,965	Area 29 NNSS	volcanic

Table A-1. Sample type and location (continued).

WGA83/NAD84 (dms)						
	Sample Date	Latitude	Longitude	Elevations (ft)	Area	Rock Type
Downgradient Locations						
Water Well C-1	1/18/2012	36 55 07.0	116 00 34.0	3,923	Area 6 NNSS	carbonate
Mifflin Well	9/30/2011	36 18 38.4	115 24 12.8	3,773	Spring Mountains	carbonate
Crystal Pool	9/30/2011	36 25 12.8	116 19 23.5	2,188	Ash Meadows	carbonate
Point of Rocks Spring	10/1/2011	36 24 05.8	116 16 16.3	2,336	Ash Meadows	carbonate
Fairbanks Spring	9/30/2011	36 29 25.7	116 20 31.5	2,249	Ash Meadows	carbonate
Water Well 8	1/18/2012	37 09 56.0	116 17 21.0	5,694	Area 18 NNSS	volcanic
Water Well 4	1/18/2012	36 54 18.0	116 01 26.0	3,601	Area 6 NNSS	volcanic
Army #1 Water Well	1/18/2012	36 35 30.0	116 02 14.0	3,153	Area 22 NNSS	carbonate
J-12 Water Well	1/18/2012	36 45 54.0	116 23 34.0	3,128	Area 25 NNSS	volcanic
Indian Springs Prison Well #4	10/20/2011	36 30 30.9	115 35 41.0	3,751	Spring Mountains	carbonate
Additional Location used for Modeling						
UE-19h	-	37 20 34.1	116 22 24.8	6,780	Area 19 NNSS	volcanic

Table A-2. Groundwater chemical and isotopic data (concentrations in mg/L).

	Temp (°C)	pH	EC (μS/cm)	Ca	Mg	Na	K	Cl	SO ₄	HCO ₃ ⁻	F	SiO ₂	Br	NO ₃ as N	TDS	δ ² H (‰)	δ ¹⁸ O (‰)	δ ¹³ C DIC (‰)	¹⁴ C DIC (pmc)	δ ¹³ C DOC (‰)	¹⁴ C DOC (pmc)	DOC	Rock Type
Upgradient Locations																							
John's Spring	12.8	7.63	256	19.2	5.45	22.6	6.74	9.9	13.2	128	0.26	54.8	0.12	0.159	200	-90.7	-12.1	-14.9	96.6	-24.3	120.1	1.60	volcanic
White Rock East Spring	10.0	7.40	234	4.78	0.28	41.5	5.40	9.5	24.4	84.0	0.33	46.1	0.06	1.76	206	-96.0	-12.7	-14.8	97.5	-23.8	106.5	3.00	volcanic
Wamp Spring	7.0	7.81	382	60.9	10.0	7.23	0.56	3.8	9.0	234	0.17	25.3	0.04	1.88	248	-84.7	-11.4	-13.0	100.6	-23.4	101.4	1.50	carbonate
Mormon Well Spring	11.0	7.72	711	79.1	47.2	14.5	0.61	14.1	23.9	455	0.12	15.5	0.18	1.18	393	-92.8	-12.5	-11.1	90.5	-21.9	96.9	2.20	carbonate
Captain Jack Spring	11.0	7.72	152	3.19	0.31	32.1	1.72	4.2	7.6	77.9	0.18	36.2	<.01	0.049	145	-102.9	-13.7	-17.2	95.3	-23.7	109.3	8.90	volcanic
Cottonwood Spring	14.0	6.63	113	5.18	0.74	17.1	2.40	2.5	5.1	63.2	0.14	51.4	0.02	0.036	107	-89.0	-11.7	-14.7	108.9	-24.9	115.5	3.00	volcanic
Tippipah Spring	12.5	7.04	215	4.51	0.34	41.5	2.95	7.3	14.8	96.7	0.21	50.2	0.06	1.34	193	-95.5	-12.6	-12.4	92.2	-22.6	108.5	1.80	volcanic
Cane Spring	13.6	7.50	497	39.3	10.8	49.3	6.77	29.4	48.6	172	0.67	57.6	0.20	5.79	345	-90.2	-11.1	-12.1	72.6	-22.2	96.0	1.30	volcanic
Deer Creek Spring #2	6.2	7.72	369	60.7	14.2	0.88	0.31	1.3	3.3	246	0.03	4.9	<.01	0.01	194	-101.5	-13.7	-11.2	95.8	-24.4	101.8	2.30	carbonate
Deer Creek Spring #1	6.0	7.76	358	69.4	6.41	0.83	0.28	1.1	1.8	235	0.03	4.8	<.01	0.05	197	-102.3	-14.0	-10.3	95.9	-22.8	106.5	1.60	carbonate
McFarland Spring	6.4	7.58	418	71.6	12.8	1.73	0.53	1.6	7.1	269	0.14	6.4	<.01	0.002	224	-99.2	-13.7	-11.2	78.1	-23.7	109.1	1.10	carbonate
Unnamed East Kawich Spring	10.3	7.01	126	12.7	2.15	8.88	1.06	3.4	8.3	58.8	0.13	34.8	0.04	<.01	102	-99.4	-13.3	-15.9	107.4	-23.3	110.4	1.91	volcanic
Upper Mack's Canyon Spring	8.8	8.45	500	60.6	33.8	1.36	0.37	1.41	5.9	334	0.03	6.4	<.01	<.01	262	-100.7	-13.6	-12.4	98.8	-20.8	102.6	2.36	carbonate
Echo 4 Well	11.0	7.79	416	69.6	13.9	1.54	0.46	1.26	9.62	278	0.14	6.6	0.013	0.22	236	-100.6	-13.7	-10.0	76.6	-19.5	101.6	0.90	carbonate

Table A-2. Groundwater chemical and isotopic data (concentrations in mg/L) (continued).

	Temp (°C)	pH	EC (μS/cm)	Ca	Mg	Na	K	Cl	SO ₄	HCO ₃ ⁻	F	SiO ₂	Br	NO ₃ as N	TDS	δ ² H (‰)	δ ¹⁸ O (‰)	δ ¹³ C DIC (‰)	¹⁴ C DIC (pmc)	δ ¹³ C DOC (‰)	¹⁴ C DOC (pmc)	DOC	Rock Type
Midgradient Locations																							
Cold Creek Spring	9.6	7.78	455	74.0	17.6	1.86	0.53	1.8	8.4	304	0.09	7.1	0.01	0.156	245	-100.3	-13.7	-10.0	68.2	-23.7	88.2	0.80	carbonate
Tramp Spring	10.0	8.00	361	27.7	3.18	45.3	1.28	9.6	13.1	187	0.15	26.4	0.12	0.54	223	-102.9	-13.2	-12.0	64.2	-23.1	76.8	0.36	volcanic
UE-29a #2	20.8	7.69	253	14.4	1.69	36.2	3.3	8.6	16.8	106	0.78	50.2	0.07	2.65	190	-92.4	-12.5	-12.6	70.8	-26.7	75.1	0.23	volcanic
Downgradient Locations																							
Water Well C-1	35.8	7.23	1040	76.6	29.2	119	14.1	34.5	66.0	561	1.14	30.9	0.08	0.08	639	-106.9	-14.1	-5.8	0.7	-23.1	45.8	0.77	carbonate
Mifflin Well	16.5	7.96	418	52.4	22.4	2.83	0.90	1.71	36.8	236	0.15	10.3	0.016	0.11	228	-103.0	-14.0	-8.6	25.0	-19.6	75.2	0.28	carbonate
Crystal Pool	30.0	7.93	670	47.9	20.7	68.7	8.10	21.2	82.0	309	1.68	22.4	0.115	0.02	386	-102.6	-13.6	-6.7	7.3	-23.5	67.1	0.36	carbonate
Point of Rocks Spring	31.5	7.81	668	48.0	20.9	66.7	7.89	21.0	80.1	307	1.48	23.2	0.115	0.12	378	-103.1	-13.6	-6.1	1.2	-25.5	66.7	0.39	carbonate
Fairbanks Spring	28.0	7.89	686	47.2	20.6	72.0	9.10	22.6	85.0	311	1.67	26.7	0.126	0.08	414	-103.3	-13.7	-5.8	1.3	-23.4	70.6	0.39	carbonate
Water Well 8	24.0	7.59	200	8.43	1.28	29.6	3.43	7.8	15.7	78.5	0.85	47.8	0.04	1.26	153	-100.3	-13.4	-13.0	24.9	-20.0	-	0.16	volcanic
Water Well 4	23.3	8.05	404	24.6	8.54	47.1	5.02	12.4	43.2	153	0.77	63.6	0.08	4.2	290	-98.7	-12.6	-10.9	18.8	-26.6	58.4	0.20	volcanic
Army #1 Water Well	30.3	7.74	523	46.6	22.1	34.2	4.94	14.9	50.6	249	0.98	20.0	0.06	0.3	311	-101.0	-13.5	-7.0	2.4	-21.5	-	0.32	carbonate
J-12 Water Well	25.3	7.81	281	14.9	2.31	40.3	4.96	7.1	22.5	116	2.01	61.7	0.02	2.03	430	-96.9	-13.1	-9.8	30.3	-22.5	68.4	0.18	volcanic
Indian Springs Prison Well #4	23.4	7.94	358	38.9	21.8	4.64	1.16	4.83	15.8	218	0.07	12.4	0.035	0.39	198	-100.9	-13.7	-8.0	5.5	-26.9	45.9	0.28	carbonate
Additional Location used for Modeling																							
UE-19h	28.9	8.17	-	33.2	1.32	63.8	2.33	8.5	38.2	198	-	54.5	-	-	-	-111.0	-14.6	-2.6	10.1	-28.5	42.6	-	volcanic

APPENDIX B: NETPATH MODELING INPUT PARAMETERS

Table B-1. Carbonate and volcanic flow paths.

Carbonate Flow Paths (Spring Mountains):			
1) McFarland Spring to Cold Creek Spring to Indian Springs Prison #4			
2) Deer Creek Spring #1 to Echo 4 Well to Mifflin Well			
Phases			
Phase Name	Formula	Dissolve / Precipitate	Isotopic Values
Calcite	CaCO ₃	both	δ ¹³ C= -1.88‰
Dolomite	CaMg(CO ₃) ₂	both	δ ¹³ C= -1.88‰
Gypsum	CaSO ₄	dissolve	
CO ₂ Gas	CO ₂ (g)	both	δ ¹³ C= -20.00‰
Constraints			
Carbon	C (as HCO ₃)		
Sulfur	S (as SO ₄)		
Calcium	Ca		
Magnesium	Mg		
Volcanic Flow Paths (NNSS):			
3) Cottonwood + UE-29a #2 + UE-19h to J-12 Water Well			
4) Tippetah Spring to Water Well 4			
Phases			
Phase Name	Formula	Dissolve / Precipitate	Isotopic Values
Calcite	CaCO ₃	both	δ ¹³ C= 0.72‰
Gypsum	CaSO ₄	dissolve	
Sodium Chloride	NaCl	dissolve	
Silicon Dioxide	SiO ₂	both	
CO ₂ Gas	CO ₂ (g)	both	δ ¹³ C= -18.00‰
Mineral Glass (tmglass)*	K _{0.368} Na _{0.383} Ca _{0.024} Mg _{0.005} Fe _{0.026} Al _{0.789} Si _{4.173} O ₁₀	dissolve	
Clay (tmclay)*	K _{0.017} Na _{0.161} Ca _{0.141} Mg _{0.138} Fe _{0.05} Al _{2.438} Si _{3.462} O ₁₀	precipitate	
Constraints			
Carbon	C (as HCO ₃)		
Sulfur	S (as SO ₄)		
Calcium	Ca		
Sodium	Na		
Chloride	Cl		
Silica	Si		
Potassium	K		

*From Farnham *et al.* (2006).

APPENDIX C: NETPATH MODELING RESULTS

Table C-1. Mass-balance changes in mmol/kg water. Positive dissolution, negative precipitation.

Flow-Path Start (up- or midgradient location)	Flow-Path End (mid- or downgradient location)	Calcite	Dolomite	Gypsum (dissolved)	CO ₂ gas	NaCl (dissolved)
Spring Mountains (carbonate)						
<u>Flow Path 1</u>						
<i>No C isotopic exchange</i>						
McFarland Spring	Cold Creek Spring	-0.15	0.20	0.01	0.20	na
Cold Creek Spring	Indian Springs Prison Well #4	-1.13	0.17	0.08	-0.77	na
<i>C isotopic exchange</i>						
McFarland Spring	Cold Creek Spring	-0.15	0.20	0.01	0.20	na
Cold Creek Spring	Indian Springs Prison Well #4	-1.13	0.17	0.08	-0.77	na
<u>Flow Path 2</u>						
<i>No C isotopic exchange and C isotopic exchange</i>						
(a) Deer Creek Spring #1	Echo 4 Well	-0.38	0.31	0.08	0.46	na
(b) Echo 4 Well	Mifflin Well	-1.06	0.35	0.28	-0.43	na
NNSS (volcanic)						
<u>Flow Path 3</u>						
<i>No C isotopic exchange and C isotopic exchange</i>						
Model 1: 0.0UE-29a#2 + .565Cottonwood + .435UE-19h	J-12 Water Well	-0.10	na	0.03	-0.29	0.06
Model 2: 0.0UE-29a#2 + .551Cottonwood + .449UE-19h	J-12 Water Well	-0.08	na	0.03	-0.34	0.05
Model 3: .475UE-29a#2 + .241Cottonwood + .284UE-19h	J-12 Water Well	-0.07	na	0.03	-0.15	0.00
Model 4: 0.0UE-29a#2 + .474Cottonwood + .526UE-19h	J-12 Water Well	0.04	na	0.00	-0.57	0.04
Model 5: 0.0UE-29a#2 + .498Cottonwood + .502UE-19h	J-12 Water Well	0.00	na	0.01	-0.50	0.04
<u>Flow Path 4</u>						
<i>No C isotopic exchange</i>						
Tippipah Spring	Water Well 4	0.16	na	0.30	0.41	0.14
<i>C isotopic exchange</i>						
Tippipah spring	Water Well 4	0.16	na	0.30	0.41	0.14
na = not applicable						

Table C-1. Mass-balance changes in mmol/kg water. Positive dissolution, negative precipitation. Geochemically unrealistic reactions are highlighted in yellow (continued).

Flow-Path Start (up- or midgradient location)	Flow-Path End (mid- or downgradient location)	SiO ₂	tmglass (dissolve)	tmclay (precipitate)	carbon exchange	$\delta^{13}\text{C}$ computed (‰)
Spring Mountains (carbonate)						
<u>Flow Path 1</u>						
<i>No C isotopic exchange</i>						
(a) McFarland Spring	Cold Creek Spring	na	na	na	0.00	-10.7
(b) Cold Creek Spring	Indian Springs Prison Well #4	na	na	na	0.00	-8.1
<i>C isotopic exchange</i>						
(a) McFarland Spring	Cold Creek Spring	na	na	na	0.47	-10.0
(b) Cold Creek Spring	Indian Springs Prison Well #4	na	na	na	0.11	-8.0
<u>Flow Path 2</u>						
<i>No C isotopic exchange and C isotopic exchange</i>						
(a) Deer Creek Spring #1	Echo 4 Well	na	na	na	0.00	-9.9
(b) Echo 4 Well	Mifflin Well	na	na	na	0.00	-7.9
NNSS (volcanic)						
<u>Flow Path 3</u>						
<i>No C isotopic exchange and C isotopic exchange</i>						
Model 1: 0.0UE-29a#2 + .565Cottonwood + .435UE-19h	J-12 Water Well	-0.60	0.18	0.00	0.00	-6.4
Model 2: 0.0UE-29a#2 + .551Cottonwood + .449UE-19h	J-12 Water Well	0.00	0.19	-0.18	0.00	-6.1
Model 3: .475UE-29a#2 + .241Cottonwood + .284UE-19h	J-12 Water Well	0.00	0.16	-0.14	0.00	-8.3
Model 4: 0.0UE-29a#2 + .474Cottonwood + .526UE-19h	J-12 Water Well	3.24	0.23	-1.18	0.00	-4.4
Model 5: 0.0UE-29a#2 + .498Cottonwood + .502UE-19h	J-12 Water Well	2.22	0.22	-0.86	0.00	-5.0
<u>Flow Path 4</u>						
<i>No C isotopic exchange</i>						
Tippipah Spring	Water Well 4	-1.40	0.13	0.31	0.00	-12.5
<i>C isotopic exchange</i>						
Tippipah spring	Water Well 4	-1.40	0.13	0.31	0.34	-11.0
na = not applicable						

Table C-1. Mass-balance changes in mmol/kg water. Positive dissolution, negative precipitation (continued).

Flow-Path Start (up- or midgradient location)	Flow-Path End (mid- or downgradient location)	$\delta^{13}\text{C}$ measured (‰)	A_0 measured (pmc)	A_0 adjusted no decay (pmc)	Downgradient ^{14}C measured (pmc)	Travel time (yrs)
Spring Mountains (carbonate)						
Flow Path 1						
<i>No C isotopic exchange</i>						
(a) McFarland Spring	Cold Creek Spring	-9.96	87.1	73.1	68.2	573
(b) Cold Creek Spring	Indian Springs Prison Well #4	-7.98	68.2	63.1	5.5	20,170
<i>C isotopic exchange</i>						
(a) McFarland Spring	Cold Creek Spring	-9.96	87.1	66.6	68.2	modern
(b) Cold Creek Spring	Indian Springs Prison Well #4	-7.98	68.2	61.5	5.5	19,960
Flow Path 2						
<i>No C isotopic exchange and C isotopic exchange</i>						
(a) Deer Creek Spring #1	Echo 4 Well	-10.01	95.9	84.3	76.6	788
(b) Echo 4 Well	Mifflin Well	-8.57	76.6	65.2	25.0	7,926
NNSS (volcanic)						
Flow Path 3						
<i>No C isotopic exchange and C isotopic exchange</i>						
Model 1: 0.0UE-29a#2 + .565Cottonwood + .435UE-19h	J-12 Water Well	-9.82	49.6	49.7	30.3	4,085
Model 2: 0.0UE-29a#2 + .551Cottonwood + .449UE-19h	J-12 Water Well	-9.82	48.2	48.3	30.3	3,858
Model 3: .475UE-29a#2 + .241Cottonwood + .284UE-19h	J-12 Water Well	-9.82	52.2	52.2	30.3	4,501
Model 4: 0.0UE-29a#2 + .474Cottonwood + .526UE-19h	J-12 Water Well	-9.82	41.4	40.9	30.3	2,470
Model 5: 0.0UE-29a#2 + .498Cottonwood + .502UE-19h	J-12 Water Well	-9.82	43.4	43.6	30.3	3,006
Flow Path 4						
<i>No C isotopic exchange</i>						
Tippipah Spring	Water Well 4	-10.94	92.2	87.7	18.8	12,721
<i>C isotopic exchange</i>						
Tippipah spring	Water Well 4	-10.94	92.2	76.4	18.8	11,586

na = not applicable

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